

Application of a Random Pore Model with Distributed Pore Closure to the Carbonation Reaction

Alberto Benedetti, Matteo Strumendo*

Department of Industrial Engineering, University of Padua, Italy
matteo.strumendo@unipd.it

The carbonation reaction between carbon dioxide and calcium oxide based solid sorbents is the basis of a promising CCS (Carbon Capture and Storage) technology. The kinetics of the carbonation reaction is characterized by several peculiarities, including incomplete conversion, a first fast stage followed by a product-layer diffusion controlled slow stage, an abrupt transition between the two stages, pore reduction and modification of the reactive/pore surfaces. Even though several kinetic models (grain models, random pore models) have been proposed to simulate the carbonation kinetics, the identification of a kinetic model capable to accurately predict the whole conversion vs time curves, particularly at short times, has been a challenging task.

In this work a random pore model accounting for a continuous sorbent pore size distribution was developed and applied to the carbonation reaction, including the reaction rate dependence on the equilibrium carbon dioxide partial pressure and the reaction order switch (from zeroth to first order). Such model is predictive once the intrinsic rate constant, the product-layer diffusivity and the initial pore size distribution are known.

The simulation results include the conversion versus time curves, as well as the evolution of the pore size distribution and of the pore and reaction surfaces over time, and are compared with experimental data of conversion over time, obtained through a high-pressure thermo-gravimetric analyzer, at a carbon dioxide pressure of 5 bar. The simulation results show that the presented model is capable to predict accurately the whole conversion-time curves, particularly at short times, both in the fast and in the product-layer diffusion regimes, and to represent the abrupt transition due to the pore closure.

1. Introduction

The Global Warming is the direct consequence of the emissions of GHGs (GreenHouse Gases) due to the human activities. According to Stocker et al. (2013) anthropogenic emissions are mostly related to large stationary sources, which mainly involve fossil fuel combustion in power plants, oil refineries and large industrial facilities. The most important anthropogenic GHG is carbon dioxide and, considering the total emissions of CO₂ per year (for large stationary sources), 78 % are produced in the power generation industry and 20 % from gas processing.

A promising technology for the carbon dioxide capture is based on the carbonation reaction ($CaO + CO_2 = CaCO_3$) using CaO based solid sorbents as a regenerable material to sequester CO₂ from combustion flue gases (Shimizu et al., 1999). However, the carbonation reaction kinetics is complex: after a fast chemically controlled initial reaction stage, a second slower reaction stage controlled by the diffusion in the product layer (CaCO₃) takes place (Barker, 1973). It has also been observed that the transition between the fast and slow regimes is abrupt (Grasa et al., 2009). Several kinetic models have been proposed to describe the CaO carbonation kinetics (Stendardo and Foscolo, 2009). However, most of them are not capable to predict correctly the conversion vs time curves and especially the sudden transition between the two regimes (Bhatia and Perlmutter, 1983a). Such sharp transition has been related to the smaller pore closure (Bhatia and Perlmutter, 1983b), therefore an accurate prediction of the CaO carbonation kinetics requires a structural model capable to represent the pore size distribution evolution over time. In this work the

Random Pore Model (RPM) independently developed by Bhatia (1985) and Sotirchos and Yu (1985) was selected and applied to the carbonation reaction. This model represents the evolution of the continuous pore size distribution of a porous network. In the carbonation reaction, as CaO is consumed a product layer of CaCO₃ is produced and interposes between the CaO solid reactant and the gas phase (CO₂). Because the molar volume of the product layer is larger than the reactant molar volume, each pore of the particle shrinks and eventually closes. Consequently, this reaction is characterized by incomplete conversion because of the pore closure. In this work, the RPM developed by Bhatia (1985) and Sotirchos and Yu (1985) is modified in order to account for the CO₂ equilibrium concentration and for the reaction rate switch from zeroth to first order (Sun et al., 2008a). A similar modelling approach was proposed by Sun et al. (2008b), however they used a discretized (rather than a continuous) pore size distribution. Differently than in Sun et al. (2008b), in this work the carbonation kinetics is simulated at short times, in order to emphasize the details of the conversion vs time curve and to check the predicted result accuracy; additionally, the time evolution of the pore size distribution and of the reaction surface during the CaO carbonation are predicted as well.

2. Pore size distribution of the CaO based sorbents

CaO sorbents were used in this work to perform carbonation tests in a thermogravimetric analyzer. Porous CaO samples were obtained from commercial CaCO₃ (150-160 μm) and calcined at 800 °C in pure N₂. The pore size distribution of the CaO samples was obtained by N₂ adsorption (BJH). The RPM of Bhatia (1985) and Sotirchos and Yu (1985) requires to determine the initial pore size distribution of the porous solid reactant (CaO). In this work a log-normal distribution is used to represent the differential pore size distribution. Defining r_0 as the initial pore radius (in Å), the log-normal pore size distribution is expressed as:

$$\varepsilon_{diff}(r_0) = \frac{\varepsilon_0}{\sqrt{2\pi}\sigma_{N_0}r_0} \exp\left\{-\frac{[\ln(r_0) - \mu_{N_0}]^2}{2\sigma_{N_0}^2}\right\} \quad (1)$$

where μ_{N_0} and σ_{N_0} are respectively the mean and the standard deviation of the normal distribution of the random variable $\ln(r_0)$; ε_0 is the initial total porosity of the sample, namely the total overlapped void fraction, according to Bhatia and Perlmutter (1980). The mean M_0 (in Å) of the log-normal distribution is related to the normal distribution parameters by:

$$M_0 = \exp\left(\mu_{N_0} + \frac{\sigma_{N_0}^2}{2}\right) \quad (2)$$

The pore length distribution $l(r_0)$ is obtained from the non overlapped pore size distribution dividing by πr_0^2 .

By fitting the experimental data of N₂ adsorption through the log-normal pore size distribution the following values of the distribution parameters were computed: $\varepsilon_0 = 0.499$, $\mu_{N_0} = 5.641$ and $\sigma_{N_0} = 0.306$.

3. The continuous random pore model applied to the carbonation reaction

The carbonation reaction is modeled in the RPM developed by Bhatia (1985) and Sotirchos and Yu (1985) for a first order irreversible reaction. In each pore, two different surfaces are identified: a reaction surface that moves inward and a pore surface that moves outward as reaction progresses. This model distinguishes the overlapped configuration from the non-overlapped one, linking the two geometries with the Avrami's equation, according to Bhatia and Perlmutter (1980). However, the carbonation reaction is reversible and, as demonstrated by Sun et al. (2008a), its reaction order switches from 0 to 1 depending on the CO₂ partial pressure. The carbonation reaction being reversible, the effect of the CO₂ partial pressure is expressed in terms of driving force with respect to the equilibrium, namely as $(p_{CO_2} - p_{CO_2,eq})$. Consequently, the RPM proposed Bhatia (1985) and Sotirchos and Yu (1985) requires to be modified to account for the reaction order switch and the equilibrium condition. Following this approach the carbonation reaction modelling is initially split into two cases, namely the first order, and the zeroth order reaction.

3.1 First order reaction

Assuming a first order reversible reaction, the surface reaction rate is expressed through:

$$\frac{\partial r_s}{\partial t} = k_s^{(1)} C_{CO_2}^{s*} \quad (3)$$

where r_s is the reaction surface radius, and $k_s^{(1)}$ is the first order rate constant. $C_{CO_2}^{s*}$ is defined as $(C_{CO_2}^s - C_{CO_2,eq})$, $C_{CO_2}^s$ being the concentration of CO₂ at the reaction front, and $C_{CO_2,eq}$ is the CO₂ equilibrium concentration which is evaluated following Baker (1962). The CO₂ concentration profile inside the solid product layer is calculated assuming pseudo-steady-state diffusion of CO₂ through the product layer (Bhatia, 1985), namely by solving the following diffusion equation for cylindrical pores:

$$\frac{\partial}{\partial r} \left(r \frac{\partial C_{CO_2}^*}{\partial r} \right) = 0 \text{ for } r_p \leq r \leq r_s \quad (4)$$

where r is the radial coordinate of each cylindrical pore, $C_{CO_2}^*$ is defined as $(C_{CO_2} - C_{CO_2,eq})$ and r_p is the pore radius. The boundary conditions of Eq. (4) are:

$$\begin{aligned} C_{CO_2}^* &= C_{CO_2}^{p*} = C_{CO_2,bulk}^* \text{ at } r = r_p \\ -D_{pl} \frac{\partial C_{CO_2}^*}{\partial r} &= k_s^{(1)} \frac{\rho_s}{M_{CaO}} C_{CO_2}^* \text{ at } r = r_s \end{aligned} \quad (5)$$

where $C_{CO_2}^{p*}$ refers to the pore interface, D_{pl} is the CO₂ molecular diffusivity in the product layer, ρ_s is the mass skeleton density of the solid reactant and M_{CaO} is the CaO molecular weight. Eq. (4), once integrated with the boundary conditions Eq. (5), provides:

$$C_{CO_2}^*(r) = \frac{C_{CO_2,bulk}^*}{1 + \frac{k_s^{(1)} \rho_s}{M_{CaO} D_{pl}} r_s \ln \left(\frac{r}{r_p} \right)} \text{ with } r_p \leq r \leq r_s \quad (6)$$

Substituting Eq. (6) into Eq. (3) at $r = r_s$ ($C_{CO_2}^*(r_s) = C_{CO_2}^{s*}$):

$$\frac{\partial r_s}{\partial t} = \frac{k_s^{(1)} C_{CO_2,bulk}^*}{1 + \frac{k_s^{(1)} \rho_s}{M_{CaO} D_{pl}} r_s \ln \left(\frac{r_s}{r_p} \right)} \quad (7)$$

3.2 Zero order reaction

According to Sun et al. (2008a), the carbonation reaction switches to zeroth order when $C_{CO_2}^s = C_{CO_2,c}$, where $C_{CO_2,c}$ is the concentration corresponding to 10 kPa. In this case the reaction rate is expressed by:

$$\frac{\partial r_s}{\partial t} = k_s^{(0)} \quad (8)$$

where $k_s^{(0)}$ is the zeroth order rate constant. The rate constant $k_s^{(0)}$ is related to the first order rate constant $k_s^{(1)}$ by $C_{CO_2,c}$ through the relation: $k_s^{(0)} = k_s^{(1)} C_{CO_2,c}$. In this case, the boundary conditions of the pseudo-steady-state CO₂ diffusion equation are:

$$\begin{aligned} C_{CO_2}^* &= C_{CO_2}^{p*} = C_{CO_2,bulk}^* \text{ at } r = r_p \\ -D_{pl} \frac{\partial C_{CO_2}^*}{\partial r} &= k_s^{(0)} \frac{\rho_s}{M_{CaO}} \text{ at } r = r_s \end{aligned} \quad (9)$$

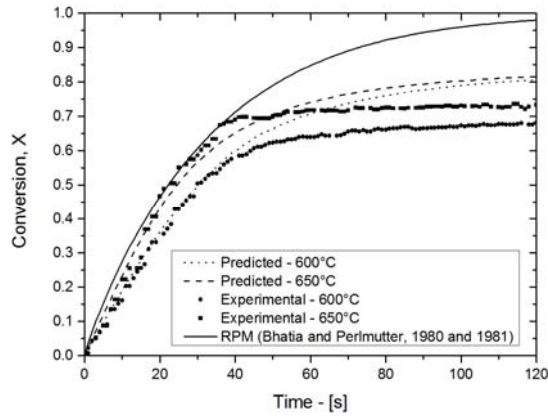


Figure 1: Comparison of the modified RPM results with experimental data (5 bar of pure CO₂)

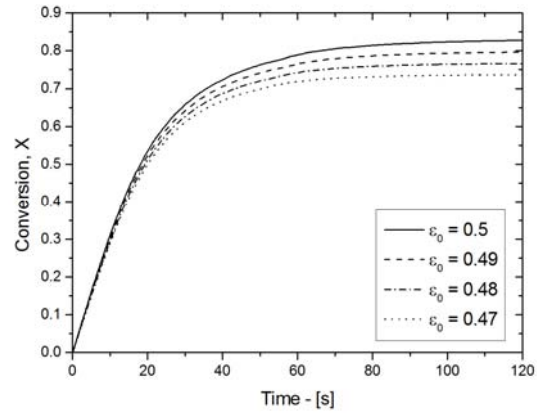


Figure 2: Effect of ε_0 on the conversion-time curves (5 bar of pure CO₂ and 650 °C)

Eq. (4), once integrated with Eq. (9), results in the following equation:

$$C_{CO_2}^*(r) = C_{CO_2, bulk}^* - \frac{k_s^{(0)} \rho_s}{M_{CaO} D_{pl}} r_s \ln\left(\frac{r}{r_p}\right) \text{ with } r_p \leq r \leq r_s \quad (10)$$

3.3 Governing equations

The previous equations (7)-(8) for r_s and (6)-(10) for the CO₂ concentration at the reaction interface are solved with the rate of change of the pore radius (Bhatia, 1985):

$$\frac{\partial r_p}{\partial t} = - \frac{(Z-1)(1-X)r_s}{[1+(Z-1)X]r_p} \left(\frac{\partial r_s}{\partial t} \right) \quad (11)$$

and with the conversion equation (Bhatia, 1985):

$$X = 1 - \frac{\exp\left[-\int_0^\infty \pi r_s^2(r_0, t) l(r_0) dr_0\right]}{1 - \varepsilon_0} \quad (12)$$

where Z is the ratio of the CaCO₃ over the CaO molar volume, ε_0 is the initial total porosity and X is the CaO conversion.

3.4 Numerical Approach

The pore length distribution is discretized in nr computational grid points following the NUMOL procedure (Schiesser, 1991). Consequently, Eqs. (7)-(8) and (11) are evaluated in each grid point. Such approach allows to build a set of $2 \times nr$ ODEs.

4. Results and discussion

In order to compare the simulation results with experimental data, TGA carbonation tests were performed using a DynTHERM MP-ST TGA by RUBOTERM GMBH. 150-160 μm particles and 5 bar of CO₂ were used to minimize intra-particle diffusion.

The modified random pore model proposed in this work is predictive (no adjustable parameters) given the initial continuous pore size distribution and the kinetic parameters (pre-exponential factor and activation energy) of the reaction rate constant and of the product layer diffusivity. As mentioned, the pore size distribution was measured by N₂ adsorption, while the parameters of the product layer diffusivity ($D_{pl} = 0.27 \exp(-E/RT)$ where E is 215 kJ mol⁻¹, R is the universal gas constant, T is in K and D_{pl} is in m² s⁻¹) were taken from Sun et al. (2008b) and the parameters of the reaction rate constant were obtained by fitting the experimental conversion vs time curves at short times.

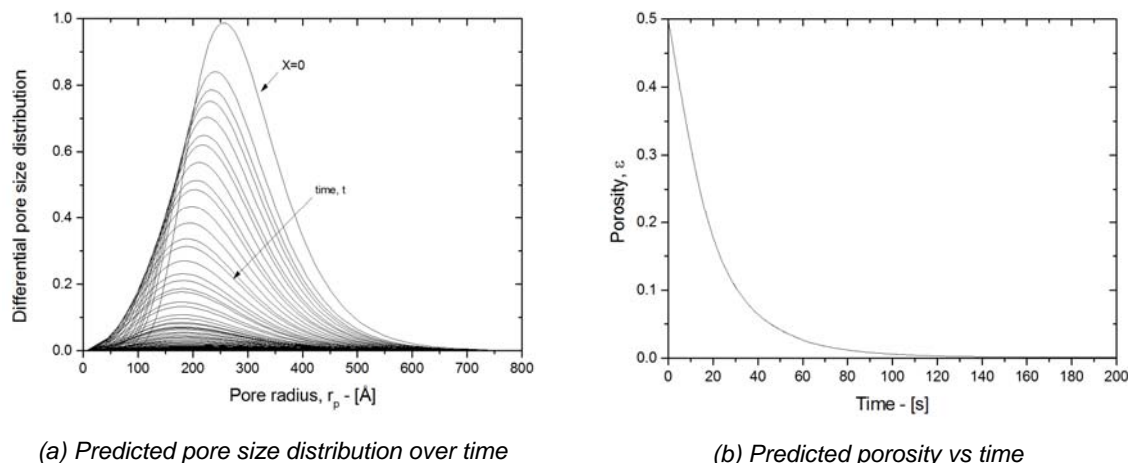


Figure 3: Predicted differential pore size distribution (\AA^{-1}) and particle porosity evolution over time (5 bar of pure CO_2 and $650\text{ }^\circ\text{C}$)

Figure 1 shows the comparison between the experimental data (carbonation temperatures equal to $600\text{ }^\circ\text{C}$ and $650\text{ }^\circ\text{C}$) and the simulation results. It is noteworthy that the modified RPM is capable to represent the whole conversion-time curve of the carbonation reaction including the sharp transition between the two regimes, even for short reaction times. Previous carbonation reaction models (except for Sun et al., 2008b) were not capable to predict simultaneously both the regimes and the sharp regime transition (an example is shown in Figure 1 for the model of Bhatia and Perlmutter, 1981 considering the temperature at $650\text{ }^\circ\text{C}$). Sun et al. (2008b) proposed an advanced carbonation reaction model, however, they obtained a reasonable agreement with experimental data only on a large time scale (namely 2,000 s).

Figure 1 shows that the final experimental conversion is overestimated by the simulation results. However, it is noticeable that the final predicted CaO conversion is rather sensitive to the initial porosity. In fact, Figure 2 shows a parametric study in which, varying the initial particle porosity within a small range (from 0.47 to 0.5) the corresponding final conversions change significantly (from 73.7 % to 83.1 %). The N_2 -adsorption data of the initial CaO samples provided a particle porosity of 0.499. The accuracy of such value, considering the high sensitivity of the conversion simulation results on the initial porosity, requires to be checked with alternative measurement techniques. Additionally, the output of the proposed model include the prediction of several structural properties. Figure 3a shows the differential pore size evolution as carbonation reaction occurs and the particle porosity is completely lost (Figure 3b) due to the pore closure after 2-3 min. Figure 4a and 4b show the trends of the total pore and reaction surface vs the CaO conversion; the predicted pore specific surface area reaches a value of less than 10 % (of the initial specific surface) at the end of the carbonation.

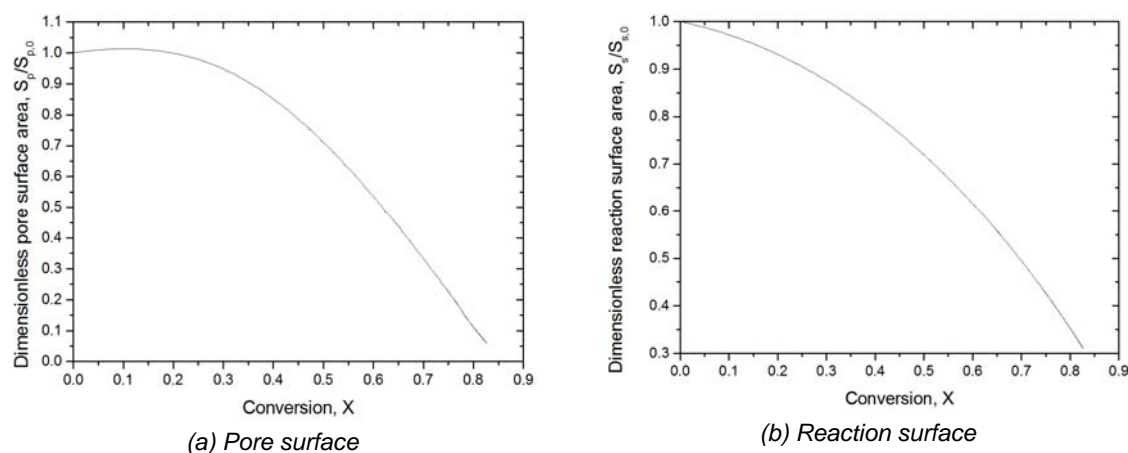


Figure 4: Prediction of the total pore and reaction surface evolution with conversion (5 bar of pure CO_2 and $650\text{ }^\circ\text{C}$)

These results were confirmed with a N₂-adsorption test on the reacted samples, which provided an experimental particle porosity of 0.015 and a reduced specific surface area ($S_p / S_{p,0}$) of 0.095.

5. Conclusions

In this work, a modified RPM was presented, based on the structural models of Bhatia (1985) and Sotirchos and Yu (1985), to represent the kinetics of the carbonation reaction, including the reaction order switch from first to zeroth and the CO₂ equilibrium concentration. The model is predictive (no adjustable parameters) given the continuous pore size distribution and the kinetic parameters of the reaction rate constant and of the product-layer diffusivity. The simulation results show that the proposed model is capable to predict the whole conversion-time curve of the carbonation reaction, particularly at short reaction times, including the sudden transition between the first fast regime and the second product layer diffusion controlled slow regime, and the pore closure due to the product layer deposition inside pores as reaction progresses. However, the final predicted conversion is highly sensitive to the initial porosity and an accurate experimental estimate of the porosity is required. Finally, the output of the proposed model include the prediction of several structural properties, namely the pore size distribution and the reaction surface evolution over time.

References

- Baker, E.H., 1962, The calcium oxide –carbon dioxide system in the pressure range 1-300 atmospheres. *Journal of Chemical Society*, 464-470.
- Barker, R., 1973, The reversibility of the reaction $\text{CaCO}_3 = \text{CaO} + \text{CO}_2$. *Journal of applied Chemistry and Biotechnology*, 23(10), 733-742.
- Bhatia S.K. Perlmutter D.D., 1980, A random pore model for fluid-solid reactions: I. Isothermal, kinetic control. *AIChE Journal*, 26(3), 379-386.
- Bhatia S.K., Perlmutter D.D., 1981, A random pore model for fluid-solid reactions: II. Diffusion and transport effects. *AIChE Journal*, 27(2), 247-254.
- Bhatia S.K., Perlmutter D.D., 1983a, Effect of the product layer on the kinetics of the CO₂-lime reaction. *AIChE Journal*, 29(1), 79-86.
- Bhatia S.K., Perlmutter D.D., 1983b, Unified treatment of structural effects in fluid-solid reactions. *AIChE Journal*, 29(2), 281-289.
- Bhatia S.K., 1985, Analysis of distributed pore closure in gas-solid reactions. *AIChE Journal* 31(4) 642-648.
- Grasa G., Murillo R., Alonso M., Abanades, J. C., 2009, Application of the random pore model to the carbonation cyclic reaction. *AIChE journal*, 55(5), 1246-1255.
- Shimizu T., Hirama T., Hosoda H., Kitano K., Inagaki M., Tejima K., 1999, A Twin Fluid-Bed Reactor for Removal of CO₂ from Combustion Processes. *Chemical Engineering Research and Design*, 77(1), 62-68.
- Sotirchos S.V., Yu, H.C 1985, Mathematical modelling of gas-solid reactions with solid product. *Chemical engineering science*, 40(11), 2039-2052.
- Stendardo S., Foscolo P.U., 2009, Carbon dioxide capture with dolomite: a model for gas-solid reaction within the grains of a particulate sorbent. *Chemical Engineering Science*, 64(10), 2343-2352.
- Stocker T. F., et al., 2013, *Climate change 2013: The physical science basis*. Intergovernmental Panel on Climate Change, Working Group I Contribution to the IPCC Fifth Assessment Report (AR5)(Cambridge Univ Press, New York).
- Sun P., Grace J.R., Lim C.J. and Anthony, E.J., 2008a, Determination of intrinsic rate constants of the CaO-CO₂ reaction. *Chemical Engineering Science*, 63(1), 47-56.
- Sun P., Grace J.R., Lim C.J. and Anthony E.J., 2008b, A discrete-pore-size-distribution-based gas–solid model and its application to the CaO + CO₂ reaction. *Chemical Engineering Science*, 63(1), 57-70.
- Schiesser W.E., 1991, *The Numerical Method of Lines: Integration of Partial Differential Equations*. Academic Press.