A modified random pore model for carbonation reaction of calcium oxide with carbon dioxide

Seyed Mohammad Mahdi Nouri, Habib Ale Ebrahim, Bahram NaserNejad

Chemical Engineering Department, Petrochemical Centre of Excellence, Amirkabir University of Technology, Tehran, Iran

Abstract

In this work, the random pore model was modified for a general concentration dependency and also bulk flow effect, in order to predict the carbonation reaction of calcium oxide with carbon dioxide. This reaction is one of the main methods for carbon dioxide capture from industrial flue gases. Different kinetic rate concentration functions were tested with the various literature experimental data for finding the best reaction constants and rate functions. Moreover, an exponential function for the diffusion of carbon dioxide through the product layer was proposed from the whole experimental conversion–time profiles.

Keywords: random pore model, calcium oxide, carbon dioxide, carbonation reaction.

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Global accumulation of CO_2 in the atmosphere has increased from 280 ppm in around 1860 to approximately 316 ppm in 1957 and rapidly to 390 ppm in 2010 [1]. Fossil fuels are the dominant form of energy utilized in the world (86%), and account for about 75% of the current anthropogenic CO_2 emission [2]. The need to reduce anthropogenic emissions of CO_2 is globally accepted and represents the driving force to reconsider the current technologies used for power generation [3].

The use of moderate temperature in the CO_2 separation step by lime has the potential to reduce efficiency penalties with respect to other methods. Within the temperature range of 400–800 °C, calcium oxide is the best choice among other metal oxides like potassium, lithium, sodium, and magnesium for reaction with CO_2. Also, the reversible carbonation/calcination reactions of calcium oxide have been proposed as the base of energy storage systems [4], and as a chemical heat pump [5]. Silaban *et al*. studied the reversibility of this reaction as the basis of a moderate temperature separation of CO_2 for the hydrogen purification [6].

A shrinking core model was applied by Johnsen *et al*. [7] to describe the carbonation reaction. Stendardo *et al*. used a modified grain model and the structural changes in the spherical grains are taken into account by the inclusion of a variable diffusivity of the gaseous reactant [8]. Bhatia and Perlmutter used a random pore model which considers the pore overlapping [9–12]. Sun et al. developed a discrete pore size distribution model with effective diffusivity in the product layer as the only fitting parameter [13]. Zero activation energy for surface reaction was obtained by Nitsch [14] and Bhatia and Perlmutter [12] and further supported by Dennis and Hayhurst [15]. Sun and his co-workers [16] obtained the activation energy of 29±4 kcal/mol for limestone and 24±6 kcal/mol for dolomite.

The reaction orders reported by different studies are not the same. Bhatia and Perlmutter claimed a first order reaction for CO_2 partial pressure of 0–10 kPa [12]. The experiments of Grasa et al. confirmed same results for up to 1 atm CO_2 partial pressure [17]. On the other hand, Kyaw *et al*. obtained a zero order for higher CO_2 partial pressures [18]. Sun et al. reported a first order for CO_2 partial pressures of less than 10 kPa, and a zero order for above this value [16].

The sudden transition of reaction rate is explained by the formation of a critical product layer by some researchers. Alvarez and Abanades estimated a product layer thickness of about 50 nm for the onset of slow reaction period [19]. They used a simple pore model and mercury porosimetry data to determine the critical product layer thickness. Barker reported a critical calcium carbonate layer thickness of 22 nm before diffusion control takes over in the progress of reaction [20]. Mess measured the product layer thickness of nonporous particles of the size range of 15–20 μm, and also a product layer thickness of 130 nm corresponding to the onset of the slow reaction period was reported [21].

In this work, carbonation reaction is investigated using a modified random pore model. The random pore model has shown good accuracy to predict some complicated gas-solid reactions such as the reaction of calcium oxide with sulphur dioxide which the solid structure changes during the reaction [22]. Data obtained by

Correspondence H.A. Ebrahim, Department of Chemical Engineering, Petrochemical Centre of Excellence, Amirkabir University of Technology, 424 Hafez Ave, Tehran, Iran.
E-mail: alebrm@aut.ac.ir
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Bhatia and Perlmutter [12], Grasa *et al*. [17] and some experiments carried out by the authors have been used to calculate the kinetic constants and diffusivity coefficient. Due to the special characteristic of the carbonation reaction in which the reaction control mechanism changes very quickly, the random pore model is not sufficient to predict this reaction and some modifications should apply to this model. These improvements consist of a general concentration dependency, and also accounting for the bulk flow phenomenon. In all the previous works for modelling the carbonation reaction of lime with CO_2, the effect of bulk flow through the solid pellet was neglected. Since carbon dioxide is the only diffusing gas and there is not any product gas in the reaction, bulk flow effects should be considered for calculating the inherent kinetic constants. Moreover, the effect of sudden shift on the reaction rate was shown by changing product layer diffusivity in this work. Bhatia and Perlmutter [12] suggested two simplified equations for the kinetically controlled region and product layer diffusion control. However, in the present work, variable product layer diffusivity is used to predict the whole conversion-time profile with the fast changes in its slope.

EXPERIMENTAL PROCEDURE

The starting material used for the experiments was calcium carbonate (Merck Art No.: 102059) which was calcined in the TGA apparatus before the carbonation experiments. The flow diagram of the system for kinetic study of the $CaO+CO_2$ reaction is presented in Figure 1. This system consists of a thermogravimeter (TG) from Rheometric Scientific (model STA-1500).

High purity CO_2 and nitrogen were used for the experiments. The pellet is put on a platinum basket cell in the TG. The system is heated under an inert gas stream (gas 1) with the rate of 20 °C/min, up to the calcination temperature (900 °C). When the calcination reaction is finished (about 2 min), the temperature decreased to the isothermal carbonation reaction temperature. After 5 min, the system is switched to a reacting gas mixture (a predefined CO_2/N_2 mixture) as gas 2 and reaction begins at the desired temperature. At this condition, the weight changes are obtained versus time by TG at a constant temperature. The conversion was obtained from the following equation from the TG profiles:

$$X = \frac{\Delta w Mw_{\mathrm{CaO}}}{w_{\mathrm{i}} Mw_{\mathrm{CO_2}} \times \mathrm{Purity}} \tag{1}$$

The nitrogen adsorption and mercury porosimetry were used to evaluate the pore size distributions of the samples (pellets after calcinations and decomposition). Nitrogen adsorption (by Autosorb-1MP from Quantachrome) determines the porous structure in the range of micro and meso pores by a 55 points test. However, larger macro-pores that are out of the detection range of nitrogen adsorption can be determined by the mercury porosimetry. By using both of above methods and combining their results, the whole pore size distributions in the range of 0.3–10000 nm can be evaluated. The pore size distribution of calcined calcium carbonate is shown in figure 2.

Model description

Consider the following general gas–solid reaction:

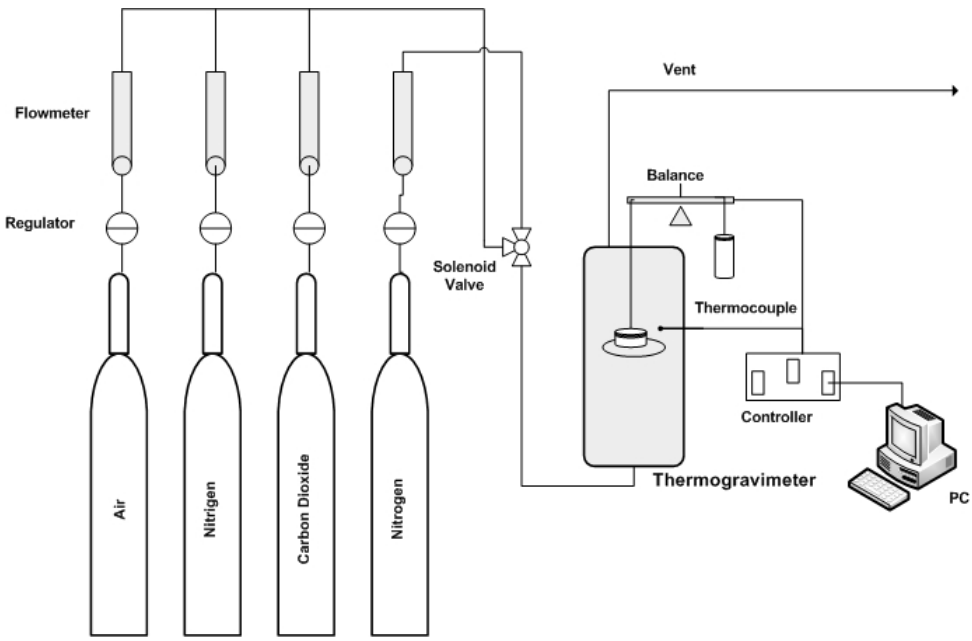

Figure 1. Experimental set up for the TG experiments.

$$A(g) + \vartheta_B B(s) \rightarrow \vartheta_C C(g) + \vartheta_D D(s) \quad (2)$$

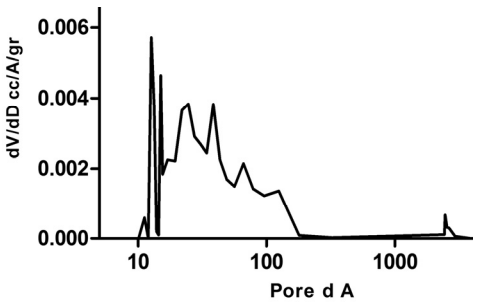

Figure 2. pore size distribution of calcined calcium carbonate.

The basic assumptions for formulating the random pore model are stated here:

(1) The reaction is initiated on the surfaces of pores in the solid B, and the nucleation of product D is rapid;

(2) The reactant B is isotropic and has no significant closed pore volume;

(3) The bulk gas concentration is constant;

(4) The pellet is isothermal;

(5) The pseudo-steady-state approximation for gas phase mass balance is valid;

(6) The pellet retains its original overall shape and size during the reaction.

The local reaction rate equation for the solid reactant is [11]:

$$\frac{dX}{dt} = \frac{k_S S_0 F(C)(1-X)\sqrt{1-\psi \ln(1-X)}}{(1-\varepsilon_0)\left[1+\frac{\beta Z}{\psi}\left(\sqrt{1-\psi \ln(1-X)}-1\right)\right]} \quad (3)$$

where β is a modified Biot modulus. ψ is the random pore model parameter which is a function of initial pore size distribution of the pellet. Z is the ratio of molar volume of the solid product to the solid reactant as follows:

$$Z = \frac{\vartheta_D \rho_B M_D}{\vartheta_B \rho_D M_B} \quad (4)$$

Using this equation, Z = 2.17 was obtained for the carbonation reaction of lime. The relation suggested by Wakao and Smith [23] is used to obtain the pore diffusion as a function of pellet porosity:

$$\delta = \frac{D_e}{D_{e0}} = \left(\frac{\varepsilon}{\varepsilon_0}\right)^2 = \left[1-\frac{(Z-1)(1-\varepsilon_0)(1-b)}{\varepsilon_0}\right]^2 \quad (5)$$

For a pellet with spherical geometry, the mass balance for gaseous reactant A is:

$$\frac{d}{dr}\left(r^2 N_A\right) = r^2 R_A \quad (6)$$

here R_A is the local rate of consumption of the fluid reactant A per unit volume. The molar flux, N_A, is given by:

$$N_A = \left(N_A + N_C\right)x_A - D_e C_T \nabla x_A \quad (7)$$

And from the stoichiometry:

$$N_A = -\vartheta_C N_C \quad (8)$$

Substituting Eq. (8) in Eq. (7) and rearranging, we get:

$$N_A = \frac{-D_e C_T dx_A / dr}{1-(1-\vartheta_C)x_A} \quad (9)$$

Combining Eqs. (6) and (9), we obtain:

$$\frac{1}{r^2}\frac{d}{dr}\left(D_e C_T r^2 \frac{dx/dr}{1-(1-\vartheta_C)x_A}\right) - R_A = 0 \quad (10)$$

Equations (3) and (10) may be written in dimensionless form as:

$$\frac{1}{y^2}\frac{\partial}{\partial y}\left(\frac{\delta y^2}{1+\theta a}\frac{\partial a}{\partial y}\right) = \frac{\phi^2 f(a) b\sqrt{1-\psi \ln b}}{1+\frac{\beta Z}{\psi}\left(\sqrt{1-\psi \ln b}-1\right)} \quad (11)$$

$$\frac{\partial b}{\partial \tau} = -\frac{f(a) b\sqrt{1-\psi \ln b}}{1+\frac{\beta Z}{\psi}\left(\sqrt{1-\psi \ln b}-1\right)} \quad (12)$$

Equations (11) and (12) show the modification of random pore model when accounting for a general concentration dependency and bulk flow effect. The initial and boundary conditions are expressed as:

$$\begin{aligned} &\tau = 0 \rightarrow \quad b = 1 \\ &y = 0 \rightarrow \quad \frac{\partial a}{\partial y} = 0 \\ &y = 1 \rightarrow \quad \frac{1+\theta}{1+\theta a}\frac{da}{dy} = Sh(1-a) \end{aligned} \quad (13)$$

Because of the sudden sharp shift from the initially fast reaction to the slower reaction rate, the random pore model should be further modified in order to predict the carbonation reaction behaviour. In order to predict the abrupt change in the carbonation reaction rate, it is assumed that D_p is a function of solid conversion. This assumption was suggested by Stendardo *et al*. [8] for the carbonation reaction of lime:

$$D_p = D_{P0} \exp(-\alpha X^{\lambda}) \quad (14)$$

The above equation is in agreement with findings of Mess *et al*. They reported that effective product layer

diffusivity decreases with time and approaches a constant value for times greater than about 600 min [21].

The effective initial diffusivity of CO_2 through porous lime is obtained by:

$$\frac{1}{D_{e0}} = \frac{1}{\varepsilon_0^2}\left(\frac{1}{D_{AM}} + \frac{1}{D_{AK}}\right) \tag{15}$$

Where D_{AM} is the molecular diffusivity of CO_2 and is estimated from the equation presented by Slattery and Bird [24]. D_{Ak} is the Knudsen diffusivity and can be determined from the following equation for the pore model [25]:

$$D_{AK} = \frac{4\bar{r}}{6}\left(\frac{8R_g T}{\pi M_A}\right)^{\frac{1}{2}} \tag{16}$$

Finally, the relations for evaluating the random pore model parameters (such as ψ and S_0) from the initial pore size distribution of the solid reactant have been presented elsewhere [26].

RESULTS AND DISCUSSION

Figure 3 shows the conversion-time data at various temperatures and CO_2 concentrations obtained from TG for calcined $CaCO_3$ pellets. As can be seen in Figure 3, after an initial rapid growth, there is a sudden transition to a much slower reaction rate regime.

Figure 4 shows the effect of bulk flow on the solid conversion. It can be seen that the bulk flow effect increases with a progress of reaction and greater importance of product layer diffusion. It is noted that when the volume of the product gas is greater than the reactant gas ($\theta > 0$), the outward bulk flow makes it more difficult for the gaseous reactant to diffuse into the interior layer of the pellet. This results in a lower overall rate of reaction. When the volume of the product gas is smaller ($\theta < 0$), the inward bulk flow speeds up the diffusion, thus increasing the overall rate of reaction. For the carbonation reaction of calcium oxide with carbon dioxide there is not any product gas, and therefore, the bulk flow effect enhances the overall rate of the reaction.

In order to investigate the kinetics of the reaction at initial stages, it is assumed that the thickness of the product layer is quite thin, so diffusion through the product layer can be neglected. With this assumption, only intrapellet diffusion and intrinsic reaction kinetics are rate controlling. Thus, Eqs. (11) and (12) can be rearranged as:

$$\frac{1}{y^2}\frac{\partial}{\partial y}\left(\frac{\delta y^2}{1+\theta a}\frac{\partial a}{\partial y}\right) = -\frac{\partial b}{\partial \tau} \tag{17}$$

$$\frac{\partial b}{\partial \tau} = -f(a)b\sqrt{1-\psi \ln b} \tag{18}$$

The solid conversion can be computed from the solid concentration as:

$$X(\tau) = 1 - 3\int_0^1 y^2 b(y,\tau)\mathrm{d}y \tag{19}$$

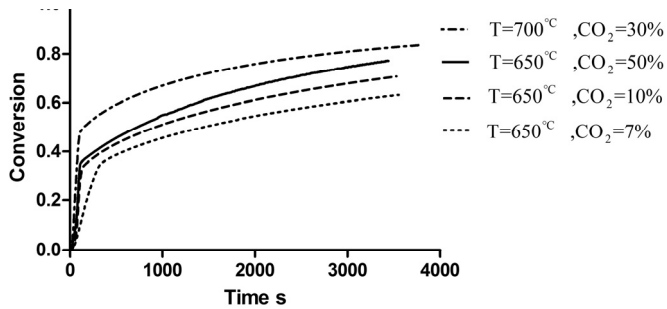

Figure 3. Conversion–time profiles of calcium oxide carbonation at different temperature and CO_2 partial pressures.

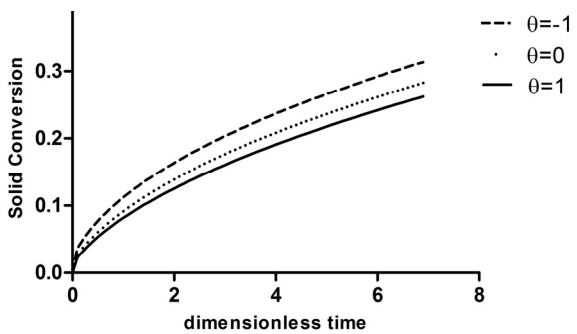

Figure 4. Effect of bulk flow on the solid conversion, β = 100, Φ = 10, ψ = 2.1.

The dimensionless solid concentration can be estimated by:

$$b = 1 - \int_0^1 f(a)\mathrm{d}\tau \tag{20}$$

Differentiation of Eq. (19) yields:

$$\frac{\mathrm{d}X}{\mathrm{d}\tau} = 3\int_0^1 y^2 f(a)\mathrm{d}y \tag{21}$$

which can be rearranged as:

$$\frac{(1-\varepsilon_0)}{S_0 3\int_0^1 y^2 f(a)\mathrm{d}y}\left[\frac{\mathrm{d}X}{\mathrm{d}t}\right]_{t\to 0} = k_s\left(C_A - C_{\mathrm{Aeq}}\right)^n \tag{22}$$

$(\mathrm{d}X/\mathrm{d}t)_{t\to 0}$ is the initial slope of experimental conversion time data. By plotting the left hand side of equation (22) against C_A for each concentration dependency, k_S can be calculated. Moreover, the deviation of points from linearity shows the accuracy of the reaction rate functions f(a) for predicting the experimental data.

The CO_2 concentration driving force is limited by the equilibrium of the carbonation reaction which is reported by Baker as [20]:

$$\log p_{\mathrm{eq}} = 7.079 - \frac{8308}{T} \tag{23}$$

This Eq. (23) shows the equilibrium pressures of about 0.07 and 0.12 atm at 700 and 800 °C, respectively. For flue gas concentration of coal combustion processes (12–15% of CO_2), the temperature above 850ºC is unfavourable for carbonation reaction.

The experimental data carried out by the TGA and the data of Bhatia and Perlmutter [12] and Grasa *et al*. [17] were used to determine the best order of reaction. Table 1 shows the correlation coefficients of each reaction order plot in Eq. (22).

As can be seen from Table 1, the fractional concentration dependency shows the best correlation. These results are in agreement with some other observations. Bhatia and Perlmutter [12] claimed a firsts order reaction for concentration of CO_2 between 0–10%. They obtained these results from an atmospheric thermogravimetric analyser. However, Sun et al. [16] and Kyaw *et al*. [18] observed a zero reaction order for higher CO_2 partial pressure. Therefore, the above proposed fractional reaction function will cover both results and change the reaction order from near one at low CO_2 partial pressures to near zero at higher CO_2 pressures. The low obtained activation energy is in agreement with the results of Bhatia [12] which did not observe any significant variation with changes in temperature. The same trend was also reported by Nitsch [14] at a higher temperature range (800–900 °C).

There is a sudden shift from the initial fast reaction rate to the slower second stage in the carbonation reaction of lime with CO_2. The data reported by some researchers show that the second stage reaction is independent of gas composition [21]. Thus, diffusion of carbon dioxide through the $CaCO_3$ product layer cannot be the rate controlling mechanism. This indicates that the reaction does not represent the simple simultaneous surface reaction and product layer diffusion process. Since the slow second stage rate is independent of CO_2 concentration, the diffusion mechanism must be in the solid phase if the rate is controlled by a product layer diffusion process.

The product layer diffusion function was evaluated from experimental data of the authors and Bhatia and Perlmutter [12], and kinetic constants were calculated. Product layer diffusion is assumed as an exponential function of solid conversion in Eq. (14) as an improvement in the random pore model.

The sudden shift in the carbonation reaction rate cannot be well predicted by the assumption of constant product layer diffusivity. Figure 5 shows a comparison between the experimental results of Bhatia and Perlmutter [12] and the model with a constant diffusivity. As can be seen in the figure, the model is not able to predict the experimental data successfully.

The values of parameters α and λ in the suggested function for D_P were obtained using trial and error at various operating temperatures. The comparison between the model predictions and the experimental conversion data for carbonation reaction is shown in

Table 1. Correlation coefficients of various reaction order functions

n	R^2		Expressions
	Bhatia's experiments	TG experiments	
1	0.994	0.885	–
2	0.954	0.735	–
0.5	0.990	0.782	–
$\frac{a}{1+k_{\mathrm{ad}}a}$	0.997	0.965	$k_s = 2.75\exp\left(\frac{7.132(\mathrm{kcal/mol})}{RT}\right)(\frac{\mathrm{cm}^4}{\mathrm{mols}})$ $k_{\mathrm{ad}} = 5000\ \frac{\mathrm{cm}^3}{\mathrm{mol}}$

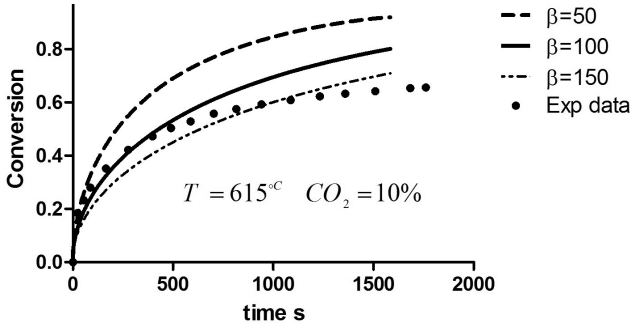

Figure 5. Comparison between the model predictions with constant product layer diffusivity and the experimental data of Bhatia and Perlmutter [12] at 615 °C and 10% CO_2.

Figures 6–8. As these Figures show, there is a very good agreement between model predictions and experimental data based on this variable product layer diffusion. Also from these figures, the product layer diffusion function is expressed as:

$$D_P = D_{P_0} \exp\left(-10X^4\right) \tag{24}$$

$$D_P \text{ at } X_f = 2.13\times10^{-7} \exp\left(-\frac{35.74\frac{\text{kcal}}{\text{mol}}}{RT}\right) \tag{25}$$

The model shows very good agreement with the data of Bhatia and Perlmutter [12] which can be seen in Figure 7. But for the TG experiment data and data of Grasa *et al*. [17], there is a small deviation between the experimental data and model results especially at the fast stage of reaction (Figures 6 and 8). Also, the transition between the fast stage of reaction and the slow stage for the data of Bhatia and Perlmutter [12] is not very sharp unlike the data of Garsa *et al*. [17] and our TG data (figure 6 and 8). It seems that the smooth form of carbonation reaction profiles in Bhatia and Perlmutter work [12] result in well prediction by the model. The macro pore texture of calcium oxide used by Bhatia seems to be responsible for his different TG profiles.

The low value of product layer diffusivity with a relatively high activation energy (35 kcal/mol), is quite a typical value associated with solid state diffusion. There are two suggested mechanisms for ion diffusion through the product layer:

A) Inward diffusion of CO_3^{2-} and outward diffusion of O^{2-} in order to maintain electroneutrality of the product layer.

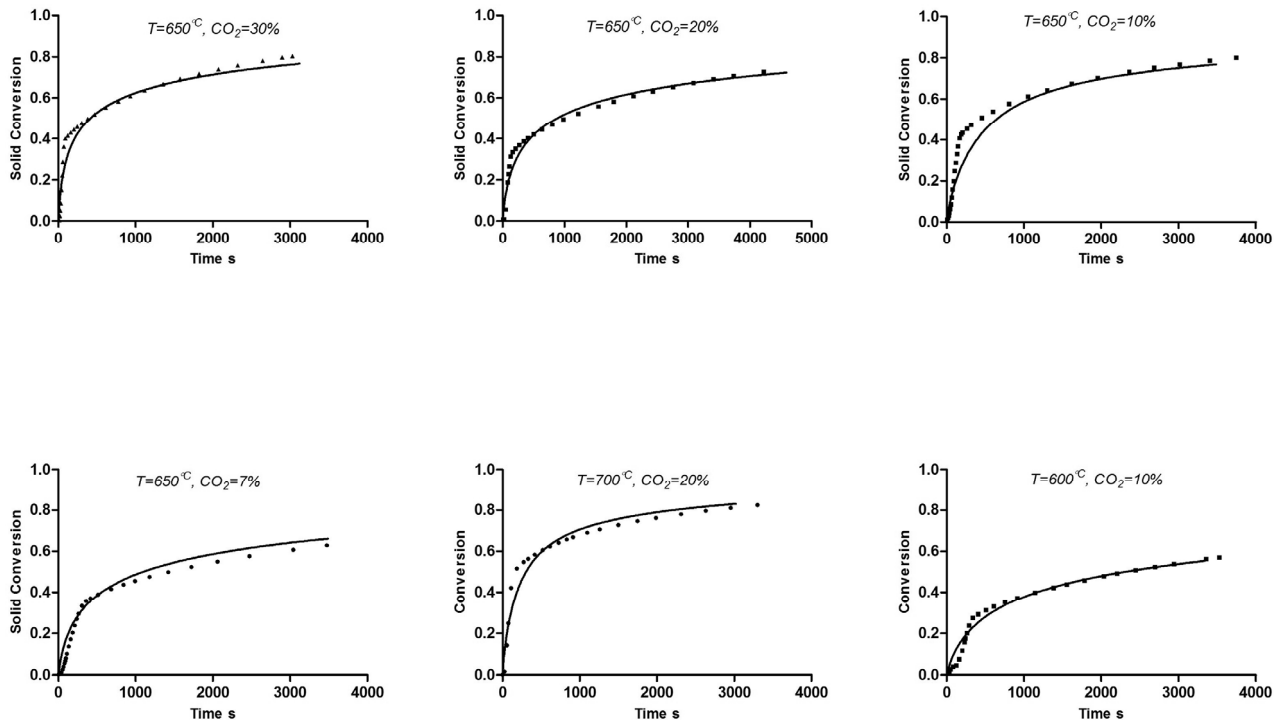

Figure 6. Comparison between the model predictions and the TG data at 650 °C and different CO_2 concentrations.

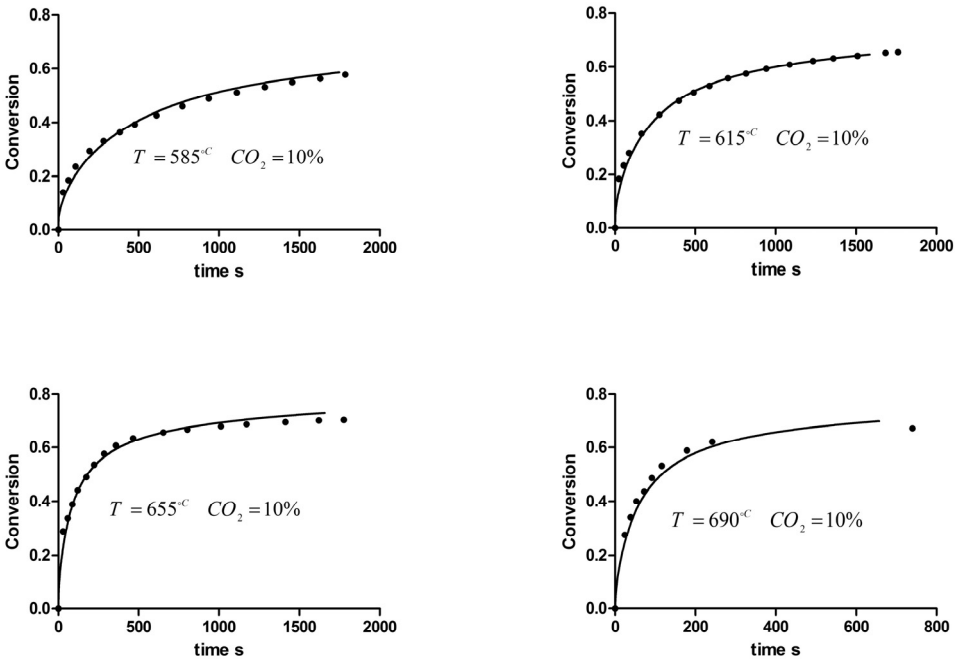

Figure 7. Comparison between improved random pore model predictions and experimental data of Bhatia and Perlmutter [12] at different temeratures.

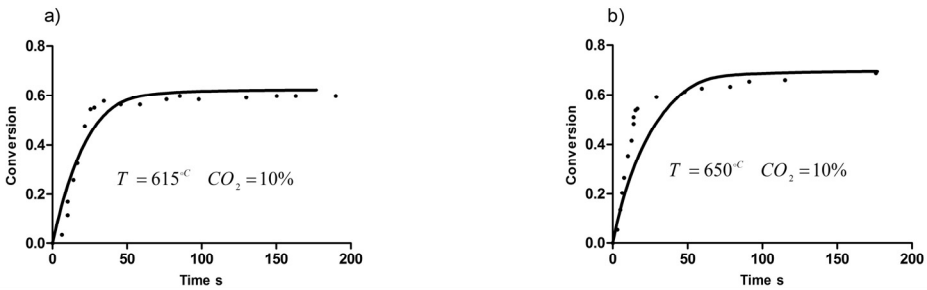

Figure 8. Comparsion between the model predictions and experimental data of Grasa et al. [17] at different temperatures.

B) Outward diffusion of Ca^{2+} and O^{2-} at the same time. Bhatia and Perlmutter suggested that the inward diffusion mechanism is dominant [12]. This idea is recently proven by Sun et al. who studied the dominating solid phase ionic transfer mechanism for diffusion of CO_2 through the $CaCO_3$ product layer [27].

Decomposition of CO_3^{2-} in the product layer can also be another diffusion mechanism. The CO_3^{2-} decomposes to a CO_2 molecule and O^{2-}. Then the CO_2 molecule moves to a vacant site in the neighbourhood. Similarly, another CO_2 molecule which decomposes elsewhere takes its place and composes the carbonate ion. By this mechanism, the CO_2 molecule moves site by site through the product layer. The possibility of this mechanism can be increased by consideration of value for decomposition heat of calcium carbonate (43.5 kcal/mol). It should be noted that there is not just one mechanism for the diffusion of CO_2 through the product layer and all of these phenomena may be involved simultaneously.

CONCLUSION

In this work, a modified random pore model for predicting the carbonation reaction of calcium oxide with carbon dioxide was developed. A general concentration rate function was considered in the modified mathematical model. Moreover, since there is not any product gas in the carbon dioxide reaction with calcium oxide, the bulk flow effect was accounted for in the random pore model. The Langmuir-Hinshelwood type rate function showed the best accuracy for the prediction of the experimental data. The kinetic constants for the reaction were calculated using this modified random pore model, and were compared with the TGA experimental data and the reported constants of Bhatia and Perlmutter [12] and Grasa *et al*. [17]. The diffusion of carbon dioxide through the product layer was also determined as an exponential function. It seems that the ionic solid phase mechanism for the product layer diffusion is dominant because of the low

values for calculated diffusivities and their high activation energy.

Nomenclature

a	C_A / C_{Ab}, dimensionless gas concentration
b	C_B / C_{B0}, dimensionless solid concentration
C_A	gas concentration in the pellet (mol/cm^3)
C_{Ab}	bulk gas concentration (mol/cm^3)
C_B	solid reactant concentration (mol/cm^3)
C_{B0}	solid reactant concentration (mol/cm^3)
C_T	total gas concentration (mol/cm^3)
D_e	effective diffusivity of gas A in the pellet (cm^2/s)
D_{e0}	initial effective diffusivity of gas A in the pellet (cm^2/s)
D_P	effective diffusivity of gas A in the product layer (cm^2/s)
D_{P_0}	initial effective diffusivity of gas A in the product layer (cm^2/s)
k_m	external mass-transfer coefficient (cm^2/s)
k_s	surface rate constant (cm^4/(mol s))
k_{ad}	adsorption coefficient
M_B	molecular weight of solid reactant (g/(g mol))
M_D	molecular weight of solid product (g/(g mol))
r	distance from the center of the pellet (cm)
R_0	radius of pellet (cm)
S_0	reaction surface area per unit volume (cm^2/cm^3)
Sh	Sherwood number for external mass transfer ($k_m R_0 / D_{e_0}$)
T	temperature (K)
t	time (s)
w	weight of solid (mg)
w_i	initial weight of solid reactant after calcination (calcium oxide) (mg)
Δw	weight gain of solid reactant during the carbonation reaction at each time t (mg)
x_i	mole fraction of species i
X	solid conversion at each time
y	dimensionless position in the pellet
Z	ratio of molar volume of solid product to solid reactant
ρ	product layer resistance, $2k_s \rho_B (1-\varepsilon_0) / M_B D_P S_0$
δ	variation ratio of the pore diffusion
ε	pellet porosity
ε_0	initial pellet porosity
θ	dimensionless bulk flow effect parameter, $(\vartheta_C - 1) x_{Ab}$
ϑ_i	stoichiometric coefficient of the reactant and product
ρ_B	true density of the solid reactant (g/cm^3)
ρ_D	true density of the solid product (g/cm^3)
τ	dimensionless time
ϕ	Thiele modulus for the pellet, $R_0 \sqrt{k_s \rho_B S_0 / M_B D_{e_0}}$
ψ	random-pore model parameter.

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IZVOD

MODIFIKOVANI MODEL NASUMIČNIH PORA ZA REAKCIJU KARBONACIJE KALCIJUM-OKSIDA UGLJEN-DIOKSIDOM

Seyed Mohammad Mahdi Nouri, Habib Ale Ebrahim, Bahram NaserNejad

Chemical Engineering Department, Petrochemical Centre of Excellence, Amirkabir University of Technology, Tehran, Iran

(Naučni rad)

U ovom radu, model nasumičnih pora je modifikovan uvođenjem funkcije zavisnosti koncentracije i uzimanjem u obzir efekta toka, da bi se predvidela reakcija karbonacije kalcijum-oksida ugljen-dioksidom. Ova reakcija je jedan od glavnih metoda za hvatanje ugljen-dioksida iz industrijskih gasova. Testirane su različite funkcije zavisnosti koncentracije, na razne literaturne eksperimentalne podatke, da bi se dobila najoptimalnija funkcija i njene konstante. Takođe, na osnovu eksperimentalno utvrđene zavisnosti konverzije od vremena reakcije predložena je eksponencijalna funkcija za koeficijent difuzije ugljen-dioksida kroz sloj proizvoda.

Ključne reči: Model nasumičnih pora • Kalcijum-oksid • Ugljen-dioksid • Reakcija karbonacije