Kinetic modeling of CO_2 capture in calcium looping process in the presence of sulfur dioxide based on random pore and fractal-like models

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ABSTRACT: Carbon dioxide is the primary greenhouse gas and its capturing by the calcium looping process is considered as one of the most promising technologies to reduce the negative effects on climate change. Since the calcium looping process is carried out at temperature higher than 700°C, it is not always possible to perform experimental investigations of the reactions taking place in industrial scales at real conditions. Therefore, in this research, two kinetic models including random pore and fractal-like models were used for the modeling of carbonation and sulfation reactions. The results showed that due to the importance of the diffusion stage in the product layer, the difference between the experimental data and the ones predicted by the random pore model increased by passing time, and this difference was more increased under higher concentrations of sulfur dioxide. On the contrary, the fractal-like model with considering variable diffusion coefficients during the reaction time, presented a better accuracy. The fractal-like model was used to predict the carbonation and sulfation reactions conversions at cycles 5, 15, and 30, showing 60, 37, and 27% carbonation conversion, and 1.6, 1.3, and 1.1% sulfation conversion, respectively. In addition, the conversions were decreased during the consecutive cycles due to the decrease of capture capacity and specific surface area of the adsorbent.

1- Introduction

The calcium looping process, which is based on the reversible reaction of carbonation-calcination between calcium oxide and calcium carbonate, has been recognized as a second-generation technology for CO_2 capture [1]. This process consists of two interconnected circulating fluidized bed reactors, namely a carbonator and a calciner. The carbonation reaction (Eq. (1)), which involves the conversion of calcium oxide to calcium carbonate at a temperature of 650 °C inside the carbonator, and the calcination reaction (Eq. (1)), which involves the decomposition of calcium carbonate into calcium oxide and carbon dioxide at a temperature higher than 900 °C inside the calciner [2, 3].

$$CaO_{(s)} + CO_{2(g)} \leftrightarrow CaCO_{3(s)} \qquad (1)$$
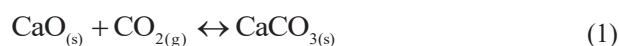
The carbonation reaction consists of two stages: the chemically controlled reaction stage (fast stage) and the diffusion-controlled stage (slow stage). Since the reaction rate is high in the initial moments, a high percentage of calcium carbonate conversion is achieved in a short period of time. By performing the carbonation reaction and reaching a critical thickness of the $CaCO_3$ layer formed on CaO, the chemically-controlled stage is transformed into the diffusion-controlled stage [4]. The presence of sulfur dioxide in the flue gas from power plants results in the formation of calcium sulfate during the carbonation process (Eq. (2)), which not only affects the absorbent's performance but also significantly alters the kinetics of carbonation and leads to deactivation of the absorbent [5].

$$CaO_{(s)} + SO_{2(g)} + 0.5O_{2(g)} \rightarrow CaSO_{4(s)} \qquad (2)$$
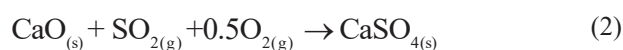
Due to the presence of corrosive SO_2 gas in the process as well as operational and equipment limitations, it is not easy to investigate the calcium looping process experimentally. Therefore, kinetic modeling and studying the effective parameters can lead to a better understanding of this process. This study aims to model the calcium looping using two different kinetic models in the presence of SO_2 gas. To validate the models used in this study, the results obtained from the two proposed models were compared with the experimental results of carbonation and sulfation reactions in the first cycle and a concentration of 500 ppm SO_2 gas provided by Manovic et al. [6]. After selecting the best kinetic model, the prediction of the conversion of carbonation and sulfation reactions in higher cycles (5, 15, and 30) and different concentrations of SO_2 gas, was investigated.

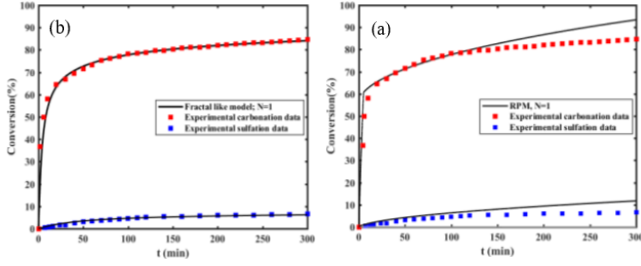*Corresponding author's email: tahmasebpoor@tabrizu.ac.ir

Fig. 1. Modeling of carbonation and sulfation at first cycle using (a) RPM (b) Fractal-like along with experimental data [6]
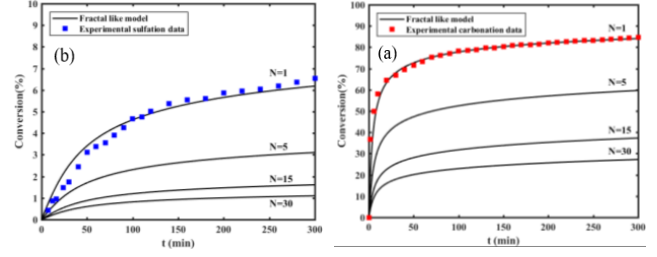

Fig. 2. Prediction of (a) carbonation and (b) sulfation reaction in cycles 5, 15 and 30 using the Fractal-like model along with experimental data in the first cycle [6]

2- Methodology

In this study, two kinetic models, including the random pore model and the fractal-like model, were utilized for the modeling of the calcium looping process. The random pore model assumes that the pores of particles are a set of uniform cylindrical shapes with random orientations. This model has been successfully applied to gas-solid reactions, including the carbonation and sulfation of CaO, and is defined by Eq. (3) [7]:

$$\frac{dX_{CaO}}{dt} = \frac{k_s S_0 C (1 - X_{CaO}) \sqrt{1 - \psi \ln(1 - X_{CaO})}}{(1 - \varepsilon)\left[1 + \dfrac{\beta Z}{\psi}\left(\sqrt{1 - \psi \ln(1 - X_{CaO})} - 1\right)\right]} \quad (3)$$

where ψ represents the internal structure parameter of the sorbent and β represents the modified Biot modulus and defined by the following equation [8]:

$$\beta = \frac{2k_S a \rho (1 - \varepsilon)}{b M_{CaO} D_P S_0} \quad (4)$$

According to Eq. (3), in a first-order reversible system, the overall reaction rate for the fast and slow stages is expressed by equations (5) and (6), respectively:

$$X_{CaO,k} = 1 - \exp\left(\frac{1 - \left(\dfrac{\tau}{2}\psi + 1\right)^2}{\psi}\right) \quad (5)$$

$$X_{CaO,D} = X_{k-D} + \left[1 - \exp\left(\frac{1}{\psi} - \frac{\left[\sqrt{1 + \beta Z \tau} - \left(1 - \dfrac{\beta Z}{\psi}\right)\right]^2 \psi}{(\beta Z)^2}\right)\right] \quad (6)$$

In the random pore model, it is assumed that Dp does not change throughout the slow stage from the beginning to the end of the reaction. However, Balasamo et al. [9] have also shown that in heterogeneous processes, the diffusion rate is a function of time. In other words, in reactions such as carbonation or sulfation, Dp should be a function of time from the beginning to the end of the reaction. In the fractal-like model, this aspect is considered using a heterogeneity parameter called h, and the modified Dp equation is presented as Eq. (7):

$$D_{PF} = D_P (t + 1)^{-h} \quad (7)$$

3- Discussion and Results

Figure 1 shows the results of the modeling for the carbonation and sulfation reactions in the first cycle, where the right graph represents modeling with the random pore model and the left graph represents modeling with the fractal-like model. Based on the experimental data for the carbonation reaction, the transition from the fast to the slow stage occurs approximately 20 minutes after the start of the reaction, which is accurately modeled by both the random pore and fractal-like models. As shown in the figure, the difference between the experimental data and the model increases towards the end of the reaction and over time, reaching 9.8% and 6% by the time 300 min for the carbonation and sulfation reactions, respectively. On the other hand, the fractal-like model accurately models the experimental data for the sulfation reaction, with a maximum error of 3% and 0.5% for the carbonation and sulfation reactions, respectively, at the end of the reaction.

As the number of carbonation-calcination cycles increases, the capacity of the sorbent for CO_2 adsorption decreases. According to Figure 2, the carbonation conversion rate predicted by the fractal-like model was 84% for Cycle 1 and 60%, 37%, and 27% for Cycles 5, 15, and 30, respectively. The sulfation conversion rate was also 6.17% for Cycle 1 and 3.1%, 1.6%, and 1.1% for Cycles 5, 15, and 30, respectively.

4- Conclusions

The random pore model and the fractal-like model were used to model the experimental data for carbonation and sulfation reactions, as well as to predict their conversion rates under different conditions. The results showed that the fractal-like model provides more accurate modeling and prediction of the conversion rates of the carbonation and sulfation reactions compared to the random pore model.

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