Study of Cao Sorbent for CO2 Capture from Flue Gases

Masoud Mofarahi[1] ,Parham Roohi ,Foroogh Farshadpoor

Chemical Engineering Department, Persian Gulf University,
Shahid Mahini Street,Bushehr, Iran

This study focuses on the CO_2 sorption from a synthetic gas mixture (3% CO_2-97% N_2) by the carbonation reaction of CaO. Experiments are carried out in a U-tube fixed bed at high temperature. The experiments are designed on the base of CO_2 adsorption dependency on the bed temperature and gas flow rate in the carbonation reaction. The CO_2 concentration profile at the outlet of The bed, is recorded by the calibrated CO_2 gas sensor (solid electrolyte type). In addition, the conversion of CaO to $CaCo_3$ is obtained in according to the bed temperature and after that, the results are applied in a proposed model. Base on this model, carbonation reaction in the fixed bed predict by the fast chemical reaction control regime. The activation energy is estimated to about 65.84, KJ/mol that it is in agreement with the other values found in the previous work for the chemical reaction control regime.

1. Introduction

Today wide researches are performing, to reduce the CO_2 emission, which are produced from the main emission sources (such as power plants, cement production, steel, refinery, etc), by CO_2 separation and geological storage (Metz et. al. 2005). In recent year's various technologies are applied or are developing regard to CO_2 capture. These technologies are classified to four main groups: post-combustion, pre-combustion, oxyfuel combustion and industrial separation. Of course, the only large scale and proven commercially available technology to separate CO_2 from combustion gases is based on amine absorption systems (Rao and Rubin, 2002). By attention to industries such as the electric producing power plants as the largest CO_2 distributor (Metz et. al. 2005), it seems necessary the design of processes that claim to be more energy efficient and cost effective than low-temperature CO_2 capture systems. The background for use of CaO as a regenerable CO_2 sorbent dates back to the 19th century (Metz et. al. 2005). Shimizu (1999) first proposed the carbonation-calcination cycle as a post-combustion system,

---

[1]Corresponding author: Tel.: +98 771 4222192; Fax: +98 771 4540376
Email address: mofarahi@pgu.ac.ir

which involved the calcination of the sorbent in a fluidized bed, by firing a fraction of the fuel with O_2/CO_2 mixtures . The overall efficiency of carbonation-calcination is higher than low temperature absorption or adsorption systems. In addition, pure CO_2 stream is produced in carbonation-calcination process (Abanades et al. 2004) and (Alvarez and Abanades, 2005). Refer to mentioned reasons the carbonation-calcination process is more beneficial than low temperature absorption or adsorption systems.In this study, a laboratory scale U-tube fixed bed is employed to investigate CO_2 separation at high temperature by use of the CaO particles. Experiments are performed on the gas mixture of 3 vol. % CO_2-97 vol. % N_2 according to the CO_2 content of gas turbines combined cycle. In addition, the effect of stream flow rate and temperature is investigated on the carbonation process. In modeling part, the experimental results are applied in a simple mathematical model (Lee ,2004) for describing the kinetic parameters of CaO-carbonation.

2. Mathematical model

In order to survey the kinetic of carbonation reaction, Lee model (Lee ,2004) is applied. Lee proposed a simple model equation to describe the kinetic of CaO carbonation, which kinetic parameters have been determined by use of CaO carbonation conversion data. This proposed model is represented by equation (1).

$$\frac{^2dX}{dt} = k(1 - \frac{X}{Xu}) \tag{1}$$

where X is the conversion of CaO; t, the time; Xu, the ultimate conversion of CaO; and k is the kinetic parameter in the model. Integration of equation (1) leads the relation between the conversion and time as represented by equation (2).

$$X = \frac{Xut}{(Xu/k) + t} \tag{2}$$

In equation (2), Lee introduced constant b as the time taken to attain half the ultimate conversion. It means that X = Xu / 2 at t = b. By substituting this relationship into equation (2), one can obtain the ultimate conversion expressed by equation (3).

$$Xu = kb \tag{3}$$

Ultimately, substitution of equation (3) to equation (2) gives the final equation for conversion of CaO as a function of time as follows:

$$X = \frac{kbt}{b + t} \tag{4}$$

Constant k and b are estimated by Arrhenius type equation as a function of temperature where T is the temperature in Kelvin.

3. Experimental section

3.1 Materials and Method

The gas mixture of 3 vol. % CO_2-97 vol. % N_2 and nitrogen (minimum purity of 99.99%) were supplied by Lion Oxygen Aria. The CaO (94 % purity) and bentonite was obtained from Pars Oxide Co. and Kohestan Group respectively.

Experiments carry out in the U-tube reactor with 30 cm length and 2.5 cm diameter with an entrance gate for the sorbent particles in the bottom of the bed. An electric furnace with capability performance at 0-1200 °C is used to support required heat for carbonation. Average diameter and bulk density of sorbent particles are 3.1± 0.1 mm and 0.68 gr/mm respectively. After the loading of CaO particles, in order to avoid the reaction between sorbent particles and CO_2 that probably remain in the system, N_2 stream is injected to the bed. This injection continues until the bed temperature reaches to the experiment temperature. In the next step, the feed gas (3% CO_2) is sent to the bed from the upper entrance. The Gas passes through the distributor plate and contacts to the sorbent particles. Then the reaction accusers between the gas and particles, and remained gas exit from the bed. Ultimately, CO_2 sensor records CO_2 concentration of remained gas.

4. Results and discussion

4.1 Experimental Results

Operating conditions of experimental runs briefly shown in table 1. As shown in this table, experiments are designed on the base of CO_2 sorption dependency on the bed temperature and gas flow rate in carbonation reaction.

Table 1. Operating conditions of experimental runs.

Run	U_g (cm.s^{-1})	T(°C)	Run	U_g (cm.s^{-1})	T(°C)
1	7.51	700	5	16.4	700
2	10.1	700	6	10.1	650
3	11.9	700	7	10.1	750
4	14.1	700			

ρ_{CO2}: 0.58 at 650°C, 0.55 at 700°C, 0.52 at 750°C

According to performed experiments, effect of feed flow rate at 700 °C and effect of the bed temperature at fixed flow rate on break through curve have been shown in figure 1 and 2 respectively. From this break through curve of CaO carbonation behavior, it can be easily speculated that during the carbonation, the bed of sorbents efficiently absorbed CO_2 fed to the system until the break point, after which the CO_2 concentration rapidly came back to the value of feed gas. As we expected with increase in the bed temperature and decrease in flow rate break through time will be increased.
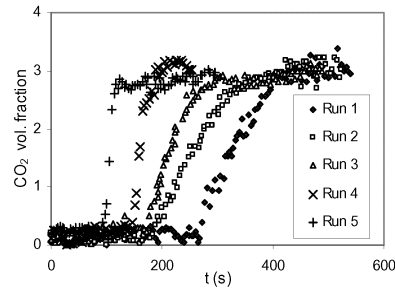
Figure 1. Experimental CO_2 concentrations measured at the outlet of the bed at five different feed gas velocities (700 °C and 3 vol. % CO_2 in the feed gas).

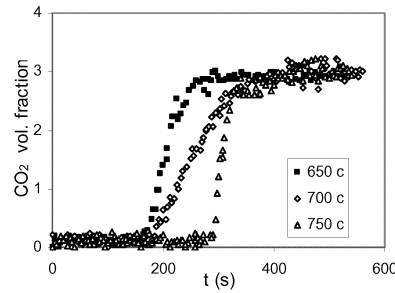*Figure 2. Experimental CO_2 concentrations measured at the exit of the bed at three different temperatures (3 vol. % CO_2 in the feed gas with velocity of 10.1 $cm.s^{-1}$).*

4.2 Data Analysis

According to mass balance in the gas phase and measuring the weight increasing at the end of carbonation, it was possible to determine this conversion by equation (5). This equation has a good agreement with the break through curve (figure 1) and other performed experiments (Shimizu et al., 1999). From equation (5), the data of carbonation conversion of CaO at the different temperature is shown in figure 5. This conversion curve shows that the rates of carbonation at the beginning of reaction are faster than subsequent times. The initial rates of CaO conversion are different depending on temperature.

$$X = \frac{Mcaco_3}{W_e} \int_0^t Q_{fg}(Cco_2, in - Cco_2, out)dt \qquad (5)$$

To determine of kinetic parameters by data fitting, equation (4) can be written in a linear form as follows:

$$\frac{1}{X} = \frac{1}{k}(\frac{1}{t}) + \frac{1}{kb} \qquad (6)$$

Figure 3 shows the linearity of conversion data when fitted to equation (6). The R-squared values at 650 °C, 700 °C and 750 °C are calculated as 0.997, 0.999 and 0.998 respectively. The values of k and b are calculated from the slopes and intercepts of the straight lines of figure 3, and the results summarized in table 2. Plot of 1/X versus 1/t is divided to two different regions (Abanades et al. 2004).
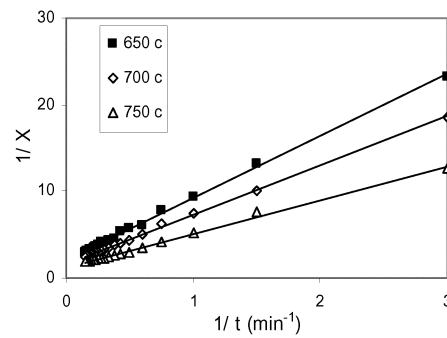

Figure 3. Plot of 1/X versus 1/t

Table 2. Kinetic parameters for used model.

T (°C)	k (min^{-1})	b (min)	Xu
650	0.124	4.70	0.58
700	0.175	3.66	0.64
750	0.284	2.66	0.75

As shown in table 2 and figure 3 the value of k increases and value of b decreases with increasing temperature. Therefore the temperature dependency of constant k could be well represented by an Arrhenius equation : $k = 627.7 \exp(-7903.9/T)$ and also for b represent by $b = 1.439 \times 10^{-2} \exp(5356.8/T)$, where T is the temperature in K. from the Arrhenius equation for k the value of activation energy is calculated as 65.64 kJ/mol .
Figure 4 shows the conversions predicted by the proposed model equation employing the parameters obtained in the chemical reaction regime at 650 and 750 °C.
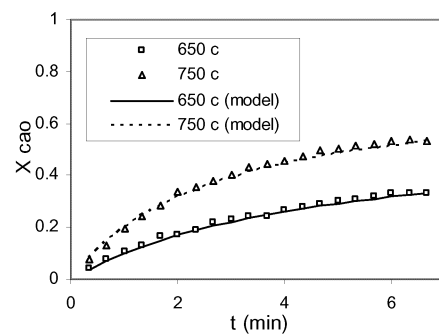

Figure 4. Prediction of conversion using model for the selected data

According to high flue gas flow rate at the industry, rapid reactivity between the sorbent and flue gas is essential. It is known that the CaO carbonation reaction involves two rate-controlling regimes. The surface chemical reaction occurs rapidly as the first rate-controlling regime. The second regime involves the counter diffusion of CO_3^{2-} and O^{2-} ions through the $CaCO_3$ product layer. The formation of an impervious layer of $CaCO_3$ slows down the reaction rate (Gupta and Fan , 2002).Therefore carbonation should take place in the fast reaction region (70-80% ultimate conversion); consequently suitable sorption is carried out at possible minimum time.

5. Conclusion

From passing the CO_2 gas mixture through the U-tube fixed bed, which contains CaO sorbents (with mentioned properties) can confirm this conclusion: the chemical reaction control regime was considered as the only rate-controlling regime in this bed. This conclusion is base on the experimental results analysis by means of a simple model. The kinetic parameters of CaO carbonation were expressed by Arrhenius type equation. The activation energy was obtained from the model as 65.64 kJ/mol. This value was found to be in a good agreement with literature (Lee ,2004).

References

Abanades J. C., Anthony E.J., Lu D.Y., Salvador C., Alvarez D., 2004, Capture of CO_2 from combustion gases in a fluidized bed of CaO, *AIChE J*. 50, 1614–1622.

Alvarez D., Abanades J. C., 2005, Pore-size and shape effects on the recarbonation performance of calcium oxide submitted to repeated calcinations /recarbonation cycles. *Energy and Fuels,* 19, 270–278.

Gupta H., Fan L.S., 2002, Carbonation-Calcination cycle using high reactivity calcium oxide for carbon dioxide separation from flue gas, Ind. Eng. Chem. Res. 41, 4035-4042 Lee D. K.,2004,An apparent kinetic model for the carbonation of calcium oxide by carbon dioxide. *Chem. Eng. J*. 100, 71–77.

Metz B., Davidson O., de Coninck H., Loos M., Meyer L., 2005, Special report on carbon dioxide capture and storage, Intergovernmental Panel on Climate Change, Cambridge University Press,.

Rao A. B, Rubin E. S., 2002 ,A technical, economic and environmental assessment of amin-based CO_2 capture technology for power plant greenhouse gas control, Env. Sci. Technol. 36, 4467-4475

Shimizu T.; Hirama T.; Hosoda H.; Kitano K.; Inagaki M.; Tejima K., 1999,A twin fluid-bed reactor for removal of CO_2 from combustion processes, *Trans. IChemE*, 77 (Part A), 62–68.