EFFECT OF SORBENT PORE VOLUME ON THE CARBONATION REACTION OF LIME WITH CO_2

S. M. M. Nouri[1*] and H. Ale Ebrahim[2]

[1]Chemical Engineering Department, Hakim Sabzevari University, Sabzevar, Khorasan, 9617976487, Iran.
Phone: + 985144012864; Fax: + 985144012850
E-mail: m.nouri@hsu.ac.ir
[2]Chemical Engineering Department, Petrochemical Centre of Excellency, Amirkabir University of Technology,
424 Hafez Ave, Tehran, 15875-4413, Iran.
Phone: 00982166499066; Fax: 00982166405847
E-mail: alebrm@aut.ac.ir

Abstract - The reaction of calcium oxide with carbon dioxide is one of the most important methods for the capture and concentration of greenhouse gas from the flue gases of industrial plants. In this work, the carbonation reaction of CaO obtained from various sources with CO_2 was investigated by a thermogravimetric method. These sources include commercial lime or CaO, $CaCO_3$, $Ca(OH)_2$, $CaC_2O_4.H_2O$, a synthesized nanoporous sorbent, limestone and acetic acid washed limestone. The effect of structural parameters of the sorbents on the reactivity and CO_2 capture capacity were studied using pore size distribution data. Also, the changes in the solid texture during the carbonation reaction were investigated. It was found that there is a direct relation between the pore volume of the sorbents and their reactivity. It was found that sintering is one of the main reasons for decreased activity in the carbonation/calcination cycles.
Keywords: CO_2+CaO reaction; Thermogravimetric Analyzer; Calcium-based sorbents; Pore size distribution.

INTRODUCTION

Global accumulation of CO_2 greenhouse gas in the atmosphere has increased from 280 ppm in around 1860 to approximately 316 ppm in 1957 and rapidly to 390 ppm in 2010 (Kenarsari *et al.*, 2013). Fossil fuels are the dominant form of energy utilized in the world (86%), and are responsible for more than 75% of the current CO_2 emission (Houghton *et al.*, 2001). The need to reduce CO_2 emissions is globally accepted and represents the driving force to reconsider the environmental aspects of current technologies used for power generation plants (Herzog, 2001).

The use of CaO as a regenerable CO_2 sorbent has been reported from several works. For example, a process using twin circulating fluidized bed reactors for the large scale carbon dioxide capture from flue gas by lime has been proposed (Shimizu *et al.*, 1999). Also, the reversible carbonation-calcination reactions of calcium oxide have been suggested as the basis of energy storage systems (Aihara *et al.*, 2001), and as the basis of a moderate temperature separation of CO_2 for hydrogen purification (Silaban, Narcida and Harrison, 1996). The effective capture of CO_2 by CaO has been demonstrated in a fluidized bed reactor or carbonation site (Abanades *et al.*, 2004). The reacted sorbent is then transferred to another fluidized bed reactor (calciner) operating at higher temperatures (>900 ºC) to produce a concentrated (>95%) CO_2 stream (Hughes *et al.*, 2005, Lu, Hughes and Anthony, 2008). Also, a relation between the extent of carbonation as a function of the number of cycles was expressed (Abanades and Alvarez, 2003).

*To whom correspondence should be addressed

There are many factors which determine the carbonation conversion, including sorbent surface area, pore size distribution, and reaction conditions like operating temperature and reaction time. However, many studies found that the capture capacity of CaO based sorbents decreased when operation cycles were extended. This is a major challenge against the future application of CaO-based technology for capturing CO_2.

There are some efforts for decreasing the fall-off in activity of the sorbent during carbonation-calcination cycles. The focus is on increasing its porosity and surface area to increase conversion, and design of the synthetic sorbents to enhance the stability. For example, a synthesized high surface area CaO sorbent was produced from precipitated calcium carbonate (Gupta and Fan, 2002). This study suggested that a mesoporous structure with a pore size range between 5-20 nm would be less susceptible to pore blockage and, thus, provide higher CO_2 capture capacity and better stability. This structure would also be able to provide sufficient surface area to ensure the rapid rate of reaction. The intermediate hydration treatment between consecutive carbonation and regeneration cycles was also employed to improve CO_2 capture capacity and enhance durability of CaO sorbents (Kuramoto et al., 2003, Manovic and Anthony, 2008).

The carbonation reaction consists of two main periods, a fast kinetic control step followed by a slow product layer diffusion control stage (Grasa et al., 2009). The first step involves a rapid heterogeneous reaction between CO_2 and CaO. In the second stage, the formation of a $CaCO_3$ product layer slows down the reaction rate considerably. The sudden transition of apparent reaction rate is explained by the formation of a critical product layer of about 50 nm for the onset of a slow reaction period (Alvarez and Abanades, 2005). Moreover, pore mouth closure and incomplete conversion phenomena can occur in the second stage due to the high molar ratio of $CaCO_3$ with respect to CaO (about 2.2). Therefore, the apparent activity of lime for the CO_2 removal reaction is an important factor for the carbonation-calcination greenhouse gas concentration process.

In this work, the carbonation reaction of CaO from various sources was investigated by a thermogravimetric method. The effect of solid textures on the reactivity and CO_2 capture capacity of the sorbents was studied using pore size distribution data. Also, the changes in the solid texture and pore size distribution during the carbonation reaction were investigated. Finally, the cyclic behavior for calcinations-carbonations of calcium carbonate was studied.

EXPERIMENTAL PROCEDURE

The flow diagram of the system for experimental study of the CaO+CO_2 reaction is presented in Figure 1. This system consists of a thermogravimetic Analyzer (TGA) from Rheometric Scientific (model STA-1500). High purity CO_2 and nitrogen were used for the experiments. Slab pellets (about 120mg in weight) were made by pressing sample powder at 5 MPa in a cylindrical die with 10 mm diameter and about 1 mm thickness. The pellet is put on the platinum basket cell in the thermogravimeter. The system is heated under an inert gas stream (gas 1) at the rate of 20 °C /min up to the desired isothermal operating temperature. After five minutes, the system is switched to a reacting gas mixture (10% CO_2/90% N_2) or gas 2 and reaction begins at the desired temperature. At this condition, the weight changes are obtained versus time by thermogravimetry at a constant temperature.
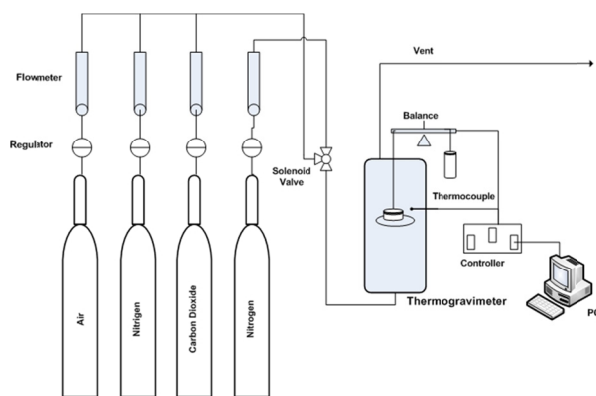

Figure 1: Flow diagram of the system for the experimental study.

For some samples (such as calcium carbonate) a calcination treatment at 900 ºC under a nitrogen stream was accomplished in the thermogravimeter prior to the above mentioned carbonation reaction. Therefore, a highly porous CaO sample was prepared in-situ for reaction with CO_2. After calcination, the temperature was decreased to the carbonation temperature and then sweep gas switched to a mixture of CO_2 and nitrogen with a pre-defined concentration by two flow meter controllers. The reaction conversion can be calculated as a function of weight gain as below:

$$X = \frac{\Delta w \times M_{wCaO}}{w_i M_{wCO_2 \times purity}} \tag{1}$$

where w_i is the initial weight of calcined CaO and

$M_w CO_2$ is the molecular weight of CO_2. Nitrogen adsorption was used to evaluate the pore size distributions of the samples (pellets after decomposition) and their specific surface areas. The pore size distributions were determined according to the HK+BJH model for micro-meso pores, respectively. Also, the BET method was used to determine the specific surface of the samples.

The various types of lime used in this work as starting materials for investigating the carbonation reaction behavior were as follows:

A) Commercial lime (CaO, Merck Art. No.102109).

B) CaO from calcination of calcium carbonate ($CaCO_3$, Merck Art. No.102059).

C) CaO from calcination of natural limestone. The natural limestone used in this work was from Abyek mine. The XRF analysis of this sorbent is shown in Table 1.

Table 1: XRF analysis of limestone sample from Abyek mine, Iran.

	CaO	Al_2O_3	SiO_2	MgO	K_2O	LOF
Composition %	52.7	0.61	0.71	1.87	0.07	45.3

D) CaO from calcination of limestone washed with acetic acid solution. For this sample, 105 g limestone was added to 500 mL of 3M acetic acid. The reaction time was about 3 h. Then it was filtered and dried at 120 ºC for 4 h.

E) CaO from decomposition of commercial calcium hydroxide ($Ca(OH)_2$, Merck Art No. 102047).

F) CaO from decomposition of commercial calcium oxalate ($CaC_2O_4.H_2O$, Aldrich).

G) CaO from calcination of a synthesized nano calcium carbonate. This sample was prepared by reaction of calcium nitrate with sodium bicarbonate solutions under ultrasonic treatment (Nouri, Ale Ebrahim and Naser Nejad, 2014).

RESULTS AND DISCUSSION

The carbonation reactions were carried out in the TGA at 650 ºC. The conversion-time profiles of different sorbents are shown in Figure 2. It is clear that the reactivity and CO_2 capture capacity of the different sorbents are not similar.

The differences in the reactivity are due to the differences in the sorbent textures. The XRD (X-Ray Diffraction) patterns show that the crystal size and structure of the sorbents are almost the same (Figure 3). Therefore, the surface reaction rate of calcium oxide with CO_2 is not different for the various sorbents. The pore size distributions of calcium oxides obtained by calcination of various sources are shown in Figure 4. Also, Table 2 shows the pore volume values and BET surface areas of the different sorbents. There is a direct relation between the parameter β (which is the pore volume of the sorbent per unit surface) and the reactivity of the sorbent, especially in the fast stage of reaction (about the first 200 s of reaction). As can be seen in Figure 2, the sorbents obtained from calcium oxalate and nano calcium carbonate show the best performance, especially in the fast stage of carbonation. The fast reaction period is practically important in order to maintain the reactor sizes economically feasible.
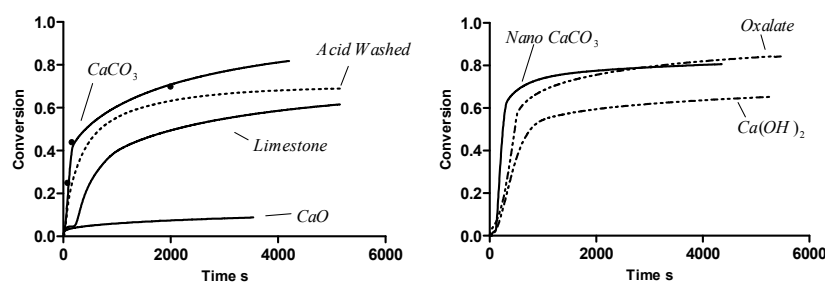

Figure 2: Conversion-time profiles for different sorbents reacting with 10% CO_2 at 650 ºC

Table 2: Structural parameters of the different sorbents.

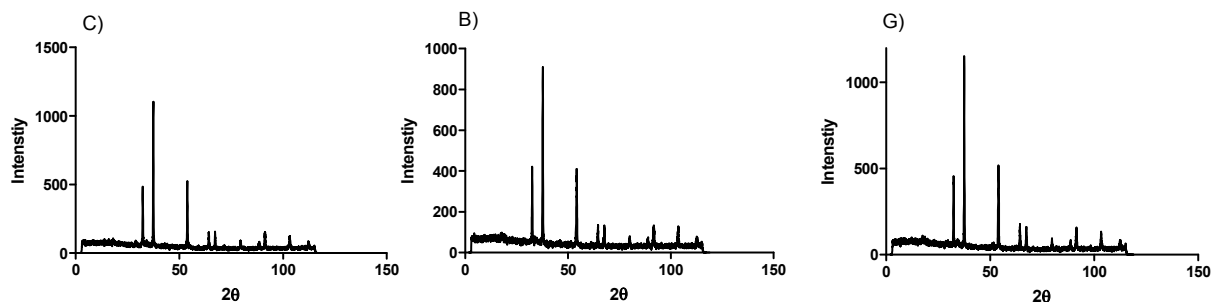|	A	B	C	D	E	F	G	B after 12 cycles
V_P (cm³/g)	0.204	0.275	0.24	0.34	0.372	0.474	0.49	0.128
S_{BET} (m²/g)	83.84	82.01	111.8	101.7	113.2	134	136.8	0.78
V_P/S_{BET} (10^6cm)	0.24	0.335	0.214	0.334	0.328	0.354	0.358	0.164

Figure 3: The XRD patterns for calcium oxides obtained from sources C, B, and G.

The overall reaction rate is a function of surface reaction kinetics, diffusion through the $CaCO_3$ product layer surrounding the CaO grains, diffusion through the macropores of the pellet, and the gas film around the pellet. In the fast kinetic control stage, the thickness of the $CaCO_3$ product layer is thin. Thus, the sorbent with higher surface area and pore volume shows higher reactivity because there is more space for the surface reaction. The sudden change in the reaction rate can be explained by the change in the morphology of the sorbent during the reaction.
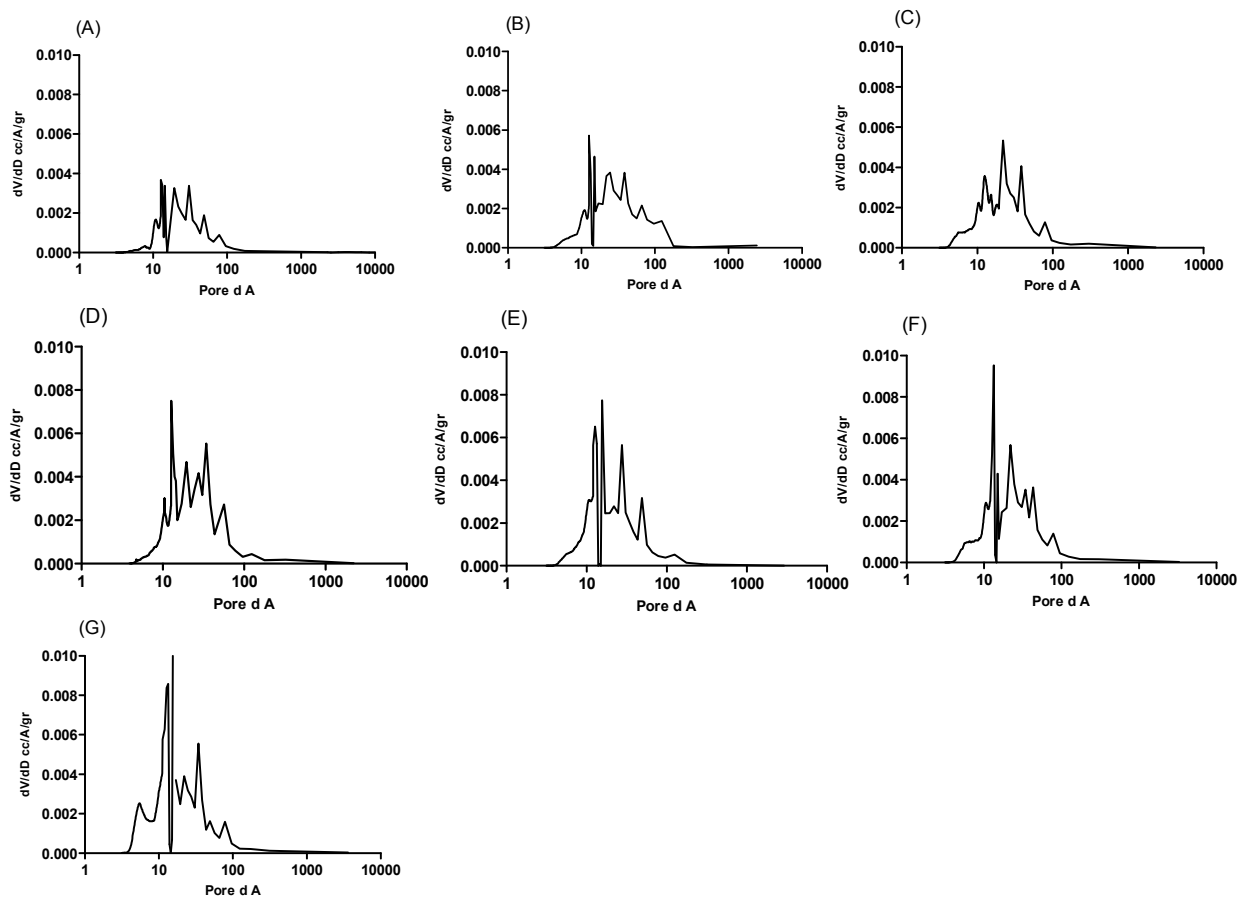

Figure 4: Pore size distributions for calcium oxides obtained from different sources (pore volume vs. pore diameter).

The effect of product layer thickness on the overall reaction rate has been investigated by some researchers (Alvarez and Abanades, 2005, Grasa *et al.*, 2008, Mess, Sarofim and Longwell, 1999). Their results showed that there is a critical thickness of the product layer which is the transition point between the fast and slow stages. Also, (Bhatia and Perlmutter, 1983) claimed that the CO_2 capture capacity in the fast stage depends only on the fraction of porosity related to the pores smaller than 100 nm. Thus, the maximum conversion in the fast stage is a function of the pore volume of the smaller pores. As can be seen in Figure 3, calcium oxides obtained from calcium oxalate and nano porous calcium carbonate show higher performance than other sorbents. The nanoporous sorbent also shows the highest reaction rate in the fast initial stage. But its reactivity in the second stage is lower which can be explained by its microporous morphology.

The change in the solid morphology during the carbonation reaction was also investigated using nitrogen adsorption. The pore volume and BET surface areas were obtained for calcined calcium carbonate (B) at the different reaction stages: a) fresh calcium oxide, b) after reaction reaches the middle of the fast stage, c) the transition point, and d) middle of the second stage (the points also can be seen in Fig. 2). Table 3 shows the structural parameters of sorbent B in these conditions. As the reaction proceeds, the pore volume per BET surface area decreased proportionally. It confirms that, upon diminishing the parameter β, we can expect lower carbon dioxide capture capacity of the sorbent. This trend cannot be seen for the pore volume and BET surface area parameters. It seems that the formation of the $CaCO_3$ product layer causes some pores with blocked bottle neck to open.

Table 3: Structural parameters of the sorbent B at different reaction points.

	Point a	Point b	Point c	Point d
V_P (cm^3/g)	0.275	0.208	0.177	0.1999
S_{BET} (m^2/g)	82.01	73.71	78.14	93.78
V_P/S_{BET} (10^6 cm)	0.335	0.282	0.2265	0.2132

Moreover, the cyclic behavior for calcination-carbonation of the lime produced from calcination of calcium carbonate (sample B) was studied by thermogravimetry. Figure 5 presents the weight changes of the sample during the calcination-carbonation periods for twelve cycles. The carbonation time was defined as 15 min for each cycle to make sure that the carbonation reaction is in the fast kinetically-

controlled stage. As can be seen in Figure 6, the calcination reaction in all the cycles goes on to completion, but decay in the carbonation reaction is considerable.
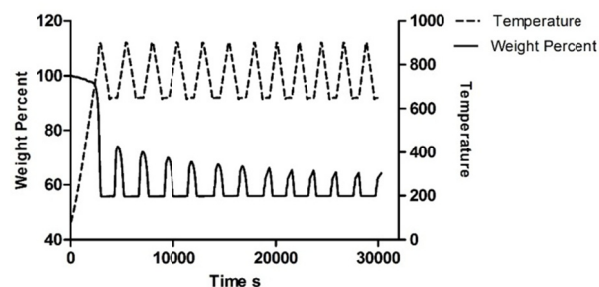

Figure 5: Study of cyclic calcination-carbonation of calcium carbonate, calcination conditions: 900 ºC and under N_2, carbonation conditions: 650 ºC and 15 min under 10% CO_2/N_2.
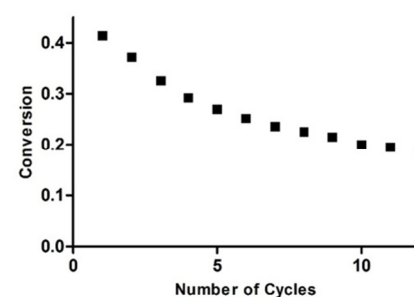

Figure 6: Effect of cycle number on the carbonation conversion at 650 ºC and 15 min under 10% CO_2/N_2 for the lime produced from calcium carbonate calcinations.

The effect of cycle number on the carbonation conversion at 650 ºC under 10% CO_2/N_2 is indicated in Figure 6. As this figure shows, the final conversion at a predefined reaction time (15 min) is changed from 43% to about 19% after twelve cycles. The results obtained in the cyclic experiments are very similar to the published works of other authors despite the differences in the sorbent morphology, operating conditions and reactor characteristics (Sun *et al.*, 2007, Fennell *et al.*, 2007, Blamey *et al.*, 2010, Alvarez and Abanades, 2005). One reason for the falloff of the carrying capacity is the closure of small pore mouths in carbonation periods that do not reopen during the next calcination (Fennell *et al.*, 2007). But it seems that sintering during the calcination period is the main reason responsible for the activity decay. The nitrogen adsorption result can also be seen in Table 2. The decay in the pore characteristics

of the sorbent during the cyclic reaction is obvious. During the calcination, the calcium carbonate decomposes to calcium oxide, causing micro and meso pores to be created. On the other hand, some of these pores sinter together creating macropores. This phenomenon decreases the activity of the sorbent during the cycles in which this decay is more rapid in the preliminary cycles. However, the difference between the final points in Gigure 6 is negligible, and thus this process approached a constant final conversion.

CONCLUSION

In this work, the rate of the carbonation reaction of lime produced from various sources was investigated by the thermogravimetric method. The increase in the porosity of these samples is due to the gaseous products evolved during the decomposition stage of the initial materials. Calcium oxide obtained from the calcination of calcium oxalate and nanoporous calcium carbonate show the best CO_2 capture capacity among the sorbents. The reactivity and CO_2 uptake capacity of the sorbents are proportionally related to their pore volumes and BET surface areas. The behavior of calcium carbonate sorbent (B) during the multiple carbonation/calcination cycles was also studied. The decay in the sorbent reactivity during the cycles is one of the major problems that is still open for investigation. It seems that, during the multiple calcinations, the pore structure of the sorbent is changed due to the sintering and its highly reactive microporous structure changes to a sintered macroporous texture.

REFERENCES

Abanades, J. C., Alvarez, D., Conversion limits in the reaction of CO_2 with lime. Energy Fuels, 17, 308-315 (2003).

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

Aihara, M., Nagai, T., Matsushita, J., Negishi, Y., Ohya, H., Development of porous solid reactant for thermal-energy storage and temperature upgrade using carbonation/decarbonation reaction. Appl. Energ., 69, 225-238 (2001).

Alvarez, D., Abanades, J. C., Determination of the critical product layer thickness in the reaction of

CaO with CO_2. Ind. Eng. Chem. Res., 44, 5608-5615 (2005).

Bhatia, S. K., Perlmutter, D. D., Effect of the product layer on the kinetics of the CO_2-lime reaction. AIChE J., 29, 79-86 (1983).

Blamey, J., Anthony, E., Wang, J., Fennell, P., The calcium looping cycle for large-scale CO_2 capture. Prog. Energ. Combust., 36, 260-279 (2010).

Fennell, P. S., Pacciani, R., Dennis, J. S., Davidson, J. F., Hayhurst, A. N., The effects of repeated cycles of calcination and carbonation on a variety of different limestones, as measured in a hot fluidized bed of sand. Energy Fuels, 21, 2072-2081 (2007).

Grasa, G., Murillo, R., Alonso, M., Abanades, J. C., Application of the random pore model to the carbonation cyclic reaction. AIChE J., 55, 1246-1255 (2009).

Grasa, G. S., Abanades, J. C., Alonso, M., González, B., Reactivity of highly cycled particles of CaO in a carbonation/calcination loop. Chem. Eng. J., 137, 561-567 (2008).

Gupta, H., Fan, L. S., Carbonation−calcination cycle using high reactivity calcium oxide for carbon dioxide separation from flue gas. Ind. Eng. Chem. Res., 41, 4035-4042 (2002)

Herzog, H. J., What future for carbon capture and sequestration? Environ. Sci. Technol., 35, 148A-153A (2001).

Houghton, J. T., Ding, Y., Griggs, D. J., Noguer, M., van der Linden, P. J., Dai, X., Maskell, K., Johnson, C., Climate Change 2001: The Scientific Basis. UK, Cambridge University Press (2001).

Hughes, R. W., Lu, D. Y., Anthony, E. J., Macchi, A., Design, process simulation and construction of an atmospheric dual fluidized bed combustion system for in situ CO_2 capture using high-temperature sorbents. Fuel Process Technol., 86, 1523-1531 (2005).

Kenarsari, S. D., Yang, D., Jiang, G., Zhang, S., Wang, J., Russell, A. G., Wei, Q., Fan, M., Review of recent advances in carbon dioxide separation and capture. RSC Adv., 3, 22739-22773 (2013).

Kuramoto, K., Fujimoto, S., Morita, A., Shibano, S., Suzuki, Y., Hatano, H., Shi-Ying, L., Harada, M., Takarada, T., Repetitive carbonation−calcination reactions of Ca-based sorbents for efficient CO_2 sorption at elevated temperatures and pressures. Ind. Eng. Chem. Res., 42, 975-981 (2003).

Lu, D. Y., Hughes, R. W., Anthony, E. J., Ca-based sorbent looping combustion for CO_2 capture in pilot-scale dual fluidized beds. Fuel Process Technol., 89, 1386-1395 (2008).

Manovic, V., Anthony, E. J., Sequential SO$_2$/CO$_2$ capture enhanced by steam reactivation of a CaO-based sorbent. Fuel, 87, 1564-1573 (2008).

Mess, D., Sarofim, A. F., Longwell, J. P., Product layer diffusion during the reaction of calcium oxide with carbon dioxide. Energy Fuels, 13, 999-1005 (1999).

Nouri, S. M. M., Ale Ebrahim, H., Naser Nejad, B., Preparation of a nano CaO sorbent for improvement the capacity for CO$_2$ capture reaction. Syn. Reac. Inorg. Met., 45, 828-833 (2014).

Shimizu, T., Hirama, T., Hosoda, H., Kitano, K., Inagaki, M., Tejima, K., A twin fluid-bed reactor for removal of CO$_2$ from combustion processes. Chem. Eng. Res. Des., 77, 62-68 (1999).

Silaban, A., Narcida, M., Harrison, D. P., Characteristics of the reversible reaction between CO$_2$(g) and calcined dolomite. Chem. Eng. Commun., 146, 149-162 (1996).

Sun, P., Grace, J., Lim, C., Anthony, E., The effect of CaO sintering on cyclic CO$_2$ capture in energy systems. AIChE J., 53, 2432-2442 (2007).