

# Sorption-Desorption Behavior of CO<sub>2</sub> on Ca<sub>3</sub>Si<sub>2</sub>O<sub>7</sub> Absorbent

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Abstract Thermodynamic analysis proves that  $Ca_3Si_2O_7$  specimen has potential to absorb and desorb  $CO_2$ . Therefore,  $Ca_3Si_2O_7$  is prepared by a solid-state reaction of  $CaCO_3$  and  $SiO_2$  starting materials. The product is characterized using X-ray diffraction (XRD) and thermo-gravimetric apparatus. The experimental results reveal that  $CO_2$  sorption level increases with increasing temperature under the condition that temperature is not more than 800 °C, with a maximum of 37.42%, and then, decreases when temperature exceeds 850 °C. Low temperature is favorable for high  $CO_2$  looping reaction capacities, of which the rate of decay is about 1.94% per cycle at 800°C while 0.63% at 750°C. 750°C is optimal temperature for  $CO_2$  sorption and desorption reaction of  $Ca_3Si_2O_7$  material.  $CO_2$  cycle temperature was diminished by using  $Ca_3Si_2O_7$  sorbent. Decreasing reaction temperature is an effective way to alleviate decaying rate.

Keyword: carbon dioxide; sorption-desorption; tricalcium silicate; TGA; melt; decay;

### 1. Introduction

Approaches of collecting CO<sub>2</sub> are numerous involving absorption with solvents [1-5], membrane separation[6-8] and use of solid sorbents such as zeolite[9-10], and so on. These techniques consume energy owing to necessary solvent much volatilization, relatively low sorbent utilization, etc., pollute environment again. Chemical even absorption of CO<sub>2</sub> by solid sorbent can be proposed as an improved technique. The process is to flow in situ flue gases through CO<sub>2</sub> solid sorbent following combustion of fossil fuel, CO2 is absorbed via a chemical reaction, then CO<sub>2</sub> can be released via atmosphere alteration resulting in an adverse chemical reaction to the preceding one for final sequestration, and simultaneously, the sorbent is regenerated and can absorb CO<sub>2</sub> again. In theory, the cycle can be performed over unlimited times. As a result, concentrated stream of CO<sub>2</sub> is yielded continuously to cater for demands of CO<sub>2</sub> utilisation. The technique can save much energy with simple process. The key point is how to find or synthesize a high-efficient solid sorbent, using its reversible chemical reactions to accomplish CO<sub>2</sub> sorption and desorption processes. Solid sorbents become attractive in recent years[5].

 $CO_2$  sorption efficiency on  $Ca_3Si_2O_7$  is high up to 45.83% according to chemical reaction equation (1).  $Ca_3Si_2O_7+3CO_2 \leftrightarrow$ 

 $3CaCO_3+2SiO_2$  (1)

Hence,  $Ca_3Si_2O_7$  is expected to be a high

efficient material to absorb  $CO_2$  and research with regard to  $Ca_3Si_2O_7$  has been rare so far. Herein, tests were carried out to determine optimal operating temperature, decay rate and specimen morphology alteration in  $CO_2$  looping cycle.

## 2. Experimental

The synthesis of Ca<sub>3</sub>Si<sub>2</sub>O<sub>7</sub> follows the reverse reaction of equation (1). Certain amounts of CaCO<sub>3</sub> agent (analytical purity) and SiO<sub>2</sub> agent (analytical purity) are weighed according to chemical stoichiometric ratio (a molar ratio, 3:2) using an electronic analytical balance, and then milled in an agate mortar. The resultant homogeneous mixture is pressed in a die via a pressing instrument into a disc shape with a diameter of 1 cm, and thickness of 2 mm at 50 Mpa, to be used in the following TGA tests performed through a TGA ( Mettler Toledo, Model TGA 851 ) instrument. Mixture flow gases of 15 vol % CO<sub>2</sub> with 85 vol % N<sub>2</sub> are purged during TGA process for CO<sub>2</sub> sorption process. The flow flux is 50 ml/min throughout. Once the adding trend becomes slow in TGA curve, N<sub>2</sub> only replaces the synthetic gases through the consequent CO<sub>2</sub> desorption duration in cycle process. A portion of the calcined specimen is grinded again for XRD measurement operated on a Siemens D500 diffractometer employing Cu/Karadiation.

# 3. Results and discussion

## **3.1 Thermodynamics of reactions**





Fig.1  $\Delta$ G plot for CO<sub>2</sub> absorption on Ca<sub>3</sub>Si<sub>2</sub>O<sub>7</sub> on different conditions

The results of thermodynamic calculations are depicted in Fig.1. In Fig.1a, pressure of CO<sub>2</sub> is constant 1 atm while in Fig.1b is variable [20]. The negative value of the Gibbs free energy indicates that the absorption process is spontaneous in nature and the degree of spontaneity of the reaction is dependent on the change of Gibbs free energy for each reactant and product ( $\Delta G$ ) in chemical reaction equation (1) under conditions that temperature and gas pressure are identical respectively before and after reaction. Fig.1 b also demonstrates CO<sub>2</sub> sorption capacity at different temperatures: at low temperature, CO<sub>2</sub> uptake capacity is high, consequently, the existing CO<sub>2</sub> pressure is low in equilibrium. According to Fig.1 a, when  $\Delta G$  is equal to be zero, reaction temperature is 574.57 K (301.42°C) in standard state. If temperature exceeds 301.42 °C,  $\Delta G$  will be positive, which is disadvantageous to CO<sub>2</sub> sorption because high negative value of change in Gibbs free energy indicates the feasible and spontaneous nature of the adsorption. However, pressure of CO<sub>2</sub> can also alter the sign of the  $\Delta G$  as mentioned above. Although Gibbs free energy gives the thermodynamic reaction potential, confirmation of the optimal temperature is

still required in the consequent experiment owing to the disregard of the reaction kinetics.

#### 3.2 Choice of CO<sub>2</sub> release temperature

CO<sub>2</sub> sorbent is expected to release CO<sub>2</sub> at low temperature as possible in order to reduce energy as well as to alleviate sintering. Therefore, the CO<sub>2</sub> release isothermal behaviors at temperature of 700, 750, 800, and 850 °C were examined by corresponding experiments. Results are depicted in Fig.2 a,b, c, and d respectively, from which, CO<sub>2</sub> release capacity can be seen is 32.69%, 32.59%, and 32.36% and 31.52%, during the period of 84, 36, 15, and 12 min at the fixed temperature of 700, 750, 800, and 850 °C respectively.

#### 3.3 XRD characterisations of Ca<sub>3</sub>Si<sub>2</sub>O<sub>7</sub> specimens

Fig.3 reveals that curve a, b, c, and d are almost identical despite different synthesis temperatures of 700, 750, 800, and 850  $^{\circ}$ C, corresponding to section 3.2, of the reaction of CaCO<sub>3</sub> and SiO<sub>2</sub> precursors according to chemical stoichiometric ratio to form Ca<sub>3</sub>Si<sub>2</sub>O<sub>7</sub> products. The peaks denoting Ca<sub>3</sub>Si<sub>2</sub>O<sub>7</sub> product intensified while the peaks belonging to









Fig.2 CO<sub>2</sub> release process by the reaction of CaCO<sub>3</sub> and SiO<sub>2</sub> starting materials with mole ratio of 3 to 2

starting materials of CaCO<sub>3</sub> and SiO<sub>2</sub> chemicals weakened. The change is remarkable for the peak of CaCO<sub>3</sub> reagent at 29.52 °, which is initially the most intensive before the reaction.



a 700°C; b 750°C; c 800°C; d 850°C Fig.3 XRD patterns of Ca<sub>3</sub>Si<sub>2</sub>O<sub>7</sub> products



# **3.4** Effects of temperatures on CO<sub>2</sub> sorption efficiencies

Fig.4 shows effects of experimental temperatures on CO<sub>2</sub> sorption efficiencies, illustrating that the CO<sub>2</sub> uptake capacities for the sorbent ascend with rising temperatures at the early stage, from 31.32% (at  $500^{\circ}$ C), 32.71% (at  $600^{\circ}$ C), 36.99% (at  $700^{\circ}$ C) to 37.42% (at  $800^{\circ}$ C), and then drops to be 31.71% (at  $850^{\circ}$ C), zero (at  $900^{\circ}$ C) respectively when temperature is over  $850^{\circ}$ C.

#### 3.5 Effect of CO<sub>2</sub> cycle times on sorption efficiencies

If a  $CO_2$  sorbent can absorb  $CO_2$  at a  $CO_2$ bearing atmosphere, and the resultant carbonated sorbent can desorb  $CO_2$  under another condition, simultaneously, the sorbent can resume its initial composition, and then, the reaction can be utilized to absorb and desorb  $CO_2$  consecutively, which is significant for  $CO_2$  separation from flue gases.  $Ca_3Si_2O_7$  is just the kind of  $CO_2$  sorbent.







Fig.4 Effects of temperatures on CO<sub>2</sub> sorption efficiencies for Ca<sub>3</sub>Si<sub>2</sub>O<sub>7</sub> specimens



Fig.5 XRD patterns of Ca<sub>3</sub>Si<sub>2</sub>O<sub>7</sub> before and after CO<sub>2</sub> absorption

Curve b in Fig.5 indicates  $Ca_3Si_2O_7$  specimen converts into  $CaCO_3$  and  $SiO_2$  after  $CO_2$  absorption, which are just the starting materials employed to synthesize  $Ca_3Si_2O_7$ . So, the reaction is reversible,  $Ca_3Si_2O_7$  can be used to absorb and desorb  $CO_2$  repeatedly. The following Fig.6 detailed  $CO_2$  sorptiondesorption cycle properties of  $Ca_3Si_2O_7$  and carbonated  $Ca_3Si_2O_7$ .

 $CO_2$  looping reaction cycles were proceeded at 750°C and 800°C as a function of time because it takes too long time for  $CO_2$  desorption at 700°C( see Fig.2 a ), and in fact,  $CO_2$  sorption temperature can be 500°C or 600°C, the cycles employed the fixed temperatures in a bid for operation convenience.

It is observed from Fig.6a that the use of  $Ca_3Si_2O_7$  specimen can absorb and desorb  $CO_2$  consecutively, though  $CO_2$  sorption capacity decayed from 37.42% to 18.01% after the specimen undergone 10 cycles. The decaying rate is 1.94% per cycle, much higher than that of CaO, 0.22% [10], whereas lower than that of lithium silicates.

#### 4. Conclusions

Temperature affects  $CO_2$  looping reaction capacities.  $CO_2$  sorption-desorption efficiencies



descend with the rising temperatures. The decaying rate is about 1.94% per cycle at 800 °C while 0.63% at 750 °C. The principal decay reason may be attributed to melt and whit sublimation of Ca<sub>3</sub>Si<sub>2</sub>O<sub>7</sub> specimen at 800 °C. 750 °C is optimal temperature for CO<sub>2</sub> sorption

and desorption reaction of  $Ca_3Si_2O_7$  material.  $CO_2$  cycle temperature was diminished by using  $Ca_3Si_2O_7$  sorbent. Decreasing reaction temperature is an effective way to alleviate decaying rate.



Fig.6 Effect of CO<sub>2</sub> cycle times on sorption efficiencies

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#### References

- Jose D. Figueroa, Timothy Fout, Sean Plasynski et al.. Advances in CO<sub>2</sub> capture technology-The U.S. Department of Energy's Carbon Sequestration Program. International Journal of Greenhouse Gas Control. 2008, 2: 9-20
- [2] B.P. Mandal, S.S. Bandyopadhyay. Absorption of carbon dioxide into aqueous blends of 2-amino-2-methyl-1-propanal and monoethanolamine. Chemical Engineering Science, 2006, 61: 5440-5447
- [3] R.Notz, N.Asprion, I.Clausen, et al. Selection and pilot plant tests of new absorbents for post-combustion carbon dioxide capture. Chemical Engineering Research anddesign. 2007, 85(4): 510-515
- [4] Mahammad R.M. Abu-zahra, Leon H.J. Schneiders, et al. CO<sub>2</sub> capture from power plants: Part I. A parametric study of the technical performance based on monoethanolamine. International Journal of Greenhouse Gas Control, 2007, 1(1):37-46

- [5] Mahammad R.M. Abu-Zahra, John P.M. Niederer, et al. CO<sub>2</sub> capture from power plants: Part II. A parametric study of the economical performance based on monoethanolamine. International Journal of Greenhouse Gas Control, 2007, 1(2):135-142
- [6] A.Kanksha, K.K.Pant, V.K. Srivastava. Carbon dioxide absorption into monoethanolamine in a continuous film contactor. Chemical Engineering Journal, 2007, 133:229-237
- [7] Aotian Xu, Aihua Yang, Stephanie Young, et al. Effect of internal coagulant on effectiveness of polyvinylidene fluoride membrane for carbon dioxide separation and absorption. Journal of Membrane Science, 2008, 311(1-2): 153-158
- [8] Clem E. Powell, Greg G. Qiao. Polymeric CO<sub>2</sub>/N<sub>2</sub> gas separation membrane for the capture of carbon dioxide from power plant flue gases. Journal of Membrane Science, 2006, 279(1-2):153-158
- [9] Sang Kompiang Wirawan, Derek Creaser. CO<sub>2</sub> adsorption on silicate-1 and cation exchanged ZSM-5 zeolites using a step change response method. Microsporous and Mesoporous Materials, 2006, 91: 196-205
- [10] Jun Zhang, Ranjeet Singh, Paul A. Webley. Alkali and alkalineearth cation exchanged chabazite zeolites for adsorption based CO<sub>2</sub> capture. Microporous and Mesoprous Materials, 2008, 111(1-3): 478-487