

GHGT-11

Synthesis of Calcium Aluminates Granule with TiO₂ Binder for High-temperature CO₂ Capture

Ching-Tsung Yu^{a,*}, Wei-chin Chen^a, Yau-Pin Chyou^a, San-Yuan Chen^b

^aInstitute of Nuclear Energy Research, Chemistry Division, Longtan 325, Taiwan

^bNational Chiao Tung University, Department of Material Science and Engineering, Hsinchu 300, Taiwan

Abstract

High-temperature CO₂ captures using powder and granule is investigated using thermogravimetric analyzer (TGA) and fixed-bed reactor (FBR). The CO₂ sorbent, Ca-Al-CO₃ powder was prepared using co-precipitation method of Ca⁺², Al⁺³ and CO₃²⁻ under alkaline conditions. The granule was fabricated by mixing Ca-Al-CO₃ powder, H₂O and w/ or w/o TiO₂ binder, followed by granulation and calcinations at 600°C. In TGA experiment, high CO₂ capacity of 45~50 wt% after 100 cycles can be achieved with powder at 750°C, while it was dramatically decayed to 40-50% only after 2-5 cycles in FBR. Alternatively, using Ca/Ti granule exhibited recovery of 80-90% for 15 cycles in TGA and 70-80% for 10 cycles in FBR, respectively. This outcome indicates that calcium aluminates granule with TiO₂ binder is competitive CO₂ sorbent.

© 2013 The Authors. Published by Elsevier Ltd.
Selection and/or peer-review under responsibility of GHGT

Keywords: Ca-Al-CO₃; Granule ; high temperature; CO₂ capture; reactor

* Corresponding author. Tel.: +886-2-82317717 ext.5103; fax: +886-3-4910419

E-mail address: ctyu@iner.gov.tw

1. Introduction

Capturing of carbon dioxide at high temperature condition has a direct advantage for abating CO₂ from concentrated sources. In terms of material stability and thermodynamic consideration, adsorption of CO₂ by solid sorbent is a specific method and environmental compatibility [1]. Among several common adsorbing materials, in terms of oxides [2], CaO-based sorbent exhibits high CO₂ adsorption capacity with average value of 50 wt% at 600-850°C. The stability of CO₂ sorption has been tested for repeat cycles in TGA, for example using powders of nano-sized CaO [3], CaTiO₃/nano-CaO [4], CaO-SiO₂ [5] and Ca-Al-Oxide [6]; pellet of limestone/kaolin [7], CaO/aluminate cement [8] and extruded particle of

Ca(OH)₂/cement [9] etc. In these studies, using pure CaO as CO₂ adsorbent, avoiding causing micropore blocking and loss of activity [10] by CaCO₃ is a main target. Therefore, it is concluded that modification of CaO-based sorbent receives a significant improvement in long-term stability and extended CO₂ sorption capability.

Utilization of layered double hydroxides (LDHs) with hydrotalcite-like structure as a template for synthesizing CO₂ sorbent has showed a vital breakthrough in multi-cycle performance. High-temperature CO₂ adsorption capability could be notably improved via replacement of Mg⁺² by Ca⁺² in Ca-Al-LDHs, which accomplished at least 90% of CaO conversion after 100 cycles [11]. The stability is maintained mainly by forming of aluminum oxides that act as the separating layer over CaO aggregates in calcined Ca-Al-Oxide [12]. However, sintering and mechanical strength are crucial considerations for using of them in a fixed-bed reactor. The sintering is still possible existed for spent sorbent, ascribing to larger molar volume of CaCO₃ covered on neighboring Ca-Al-Oxide kernels, resulting to de-activate sorbent. Due to poor heat transfer developed within nascent CaO structure [13], the heat expansion create asymmetric stress difference in grains, leading to crushed particle. Thus Ca/Al oxides boundary should be isolated and/or bonding with suitable inorganic binder as supported material.

TiO₂ is a commercial available material with hydrophilic attraction force with Ca⁺² and Al⁺³ under alkaline condition, emerging an economically competitive potential for as a binder of Ca/Al LDHs. In addition, a heat-resistance compound of CaTiO₃ can be formed under high temperature calcinations, helping to acquire a satisfied CO₂ capture activity. In this work, the solid sorbents of Ca-Al-CO₃ with powder and granule form were prepared using coprecipitation method. The pore property, crystalline and morphology of these materials were examined by BET, XRD and SEM. A fixed-bed reactor was built up for testing CO₂ capture performance at 600-850°C, using TGA and fixed-bed adsorption of CO₂ on sorbents made of Ca/Al granule with TiO₂ binder. Multi-cycling test method was applied for inspection of CO₂ sorption stability in both reactors.

2. Experimental

2.1. Synthesis of sorbents

The CaO based sorbents were prepared by precipitation of inorganic ions of Ca⁺², Al⁺³ and CO₃²⁻ under alkaline conditions. Raw materials of Ca(OAc)₂·H₂O, Al(NO₃)₃·9H₂O, NaOH and Na₂CO₃ were purchased from Merck Co. TiO₂ powder (Degussa P25) is used as a binder for forming granule.

Fig. 1 depicts the synthesis procedure of Ca-Al-CO₃ powder and granule. In this method, cationic solution of Ca⁺²/Al⁺³, with molar ratio of 7:1 of Ca(OAc)₂ and Al(NO₃)₃, was prepared by dissolution of both chemicals in Di-H₂O. The precipitate of Ca/Al carbonates was formed after addition of 0.16 mol NaOH with 0.01 mol Na₂CO₃ in stirred Ca⁺²/Al⁺³ solutions and followed by filtration to obtain layered double hydroxides (LDHs) powder. These LDHs were further calcined at 600°C for producing Ca-Al-CO₃ powder, which is used as raw material for granulation. The granule can be fabricated by either simply adding of H₂O into Ca-Al-CO₃ powder or with extra TiO₂ binder. In the latter case, granule was made of different weight ratio x of Ca-Al-CO₃ (Ca) powder and TiO₂ (Ti) binder, with x from 1 to 6. The obtained cylindrical granule with an average size of 3 mm (diameter) by 5 mm (length) that was shaped by appropriate apparatus. The Ca/Ti granules were calcined at 600~850°C for identifying the specific patterns. The characteristics of surface area, morphology/particle size and crystalline of prepared sample were determined by BET (Quantchrome), SEM (Hitachi) and PXRD (Bruker), respectively.

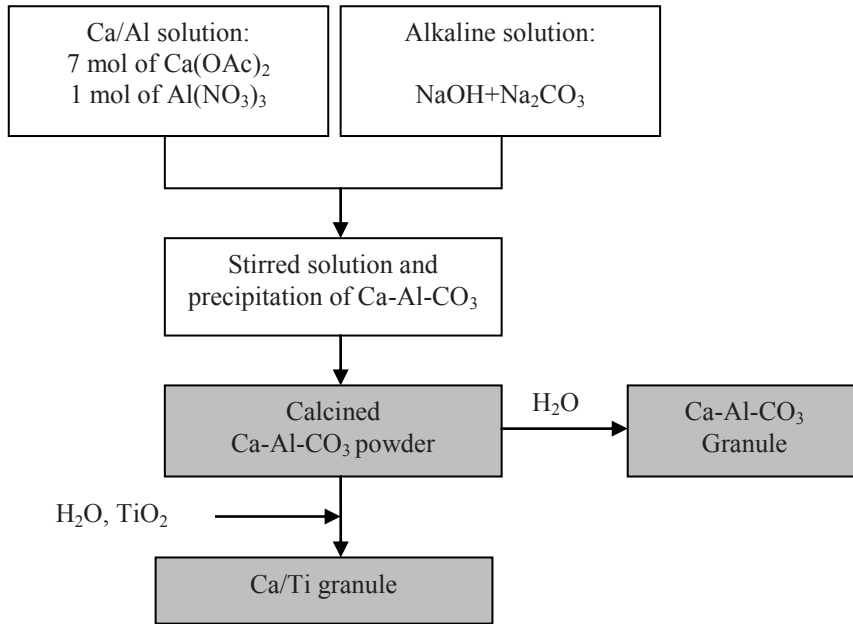


Fig.1. Flow chart of preparing Ca-Al-CO₃ powder, granule and Ca/Ti granule.

2.2 CO₂ sorption experiment

Thermogravimetric analysis is used to investigate CO₂ capture activity over sorbents at the same temperature of 750°C for 1 hour adsorption at 100% CO₂ (50 mL/min) and 0.5 hour desorption at 100% N₂ (50 mL/min) conditions, respectively. The capture capacity (wt%, g CO₂/g sorbent) in TGA was recorded by balance and expressed in terms of sorption weight with respect to the sorbent weight.

Referring to Fig.2, illustrating of a fixed-bed reactor (FBR) for CO₂ adsorption experiment operated at 600-850°C and ambient pressure. The testing gas stream is 40% CO₂ (N₂ balance, 2L/min), which is fed to a 1-inch quartz column packed with the adsorbent. After CO₂ uptake on CaO, the passing gas was cooling down together with CO₂ volume monitored by a Non-dispersive Infrared (NDIR) detector. The average integral method on the values of CO₂ volume obtained at each cycles was applied for the estimation of absorption capacity [14]. In this approximation, CO₂ sorption volume was calculated by integrating the volume difference of CO₂ (ΔV_{CO2}) with time, which was based on 90% breakthrough over the outlet of column. CO₂ capacity (g) was estimated by molar volume at 25°C via an ideal gas equation. The CO₂ specific absorption W(t) as a function of cycle was then obtained according to the formula:

$$W(t) = \frac{(\int_{-1}^t \Delta V) \cdot 44 / 24.5}{W_{sorbent}} ; i = cycles \quad \dots\dots\dots \text{Formula (I)}$$

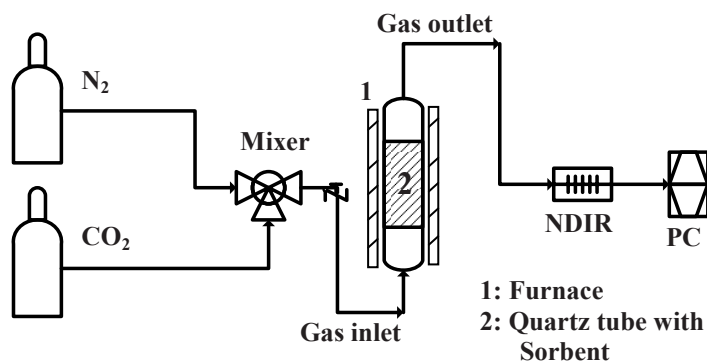


Fig.2. Schematic of a fixed-bed reactor (FBR) for CO₂ adsorption experiment.

3. Results and discussion

3.1 Characterization of sorbents

Microscopic characters of TiO₂ and calcined samples were shown in Table 1. The binder, TiO₂ has the smallest value of particle size, the next of Ca-Al-CO₃ powder and the last of two granules. BET data indicated that both of powder and granule exhibited mesoporous character with a pore size value of 14~24 nm and the surface area was around 17~23 m²/g [15]. Extruded Ca-Al-CO₃ granule shows a slightly smaller surface area than powder. However, pore volume and pore size of Ca/Ti granule were enhanced by incorporating of TiO₂. The hydroxyl group on the surface of TiO₂ provides a linking force between Ca⁺²/Al⁺³ ions and OH⁻, which promotes a separated layer of TiO₂ formed on surround of Ca-Al-CO₃ aggregates. The carbonation reaction of CO₂ and TiO₂ is unavailable in 750°C; therefore, with the advantage using TiO₂ as binder, the higher surface area of granule than powder is beneficial for increasing adsorption performance of sorbent.

Table 1. Microscopic characteristics of sorbents

Sorbents	Particle size	Surface Area, m ² /g	Pore Volume, cc/g	Pore Diameter, nm
TiO ₂ powder	40 nm	63.8	0.25	3.0
Ca-Al-CO ₃ powder	200 μm	17.3	0.06	14.6
Ca-Al-CO ₃ granule	3 mm× 5 mm (diameter×length)	12.9	0.04	23.9
Granule with x= Ca/Ti; x=4	3 mm× 5 mm (diameter×length)	23.0	0.06~0.16	15.0

Fig. 3 illustrated the SEM image of calcined Ca/Ti granule with a smooth appearance and compacted formation. At the same experimental conditions, granule made from the absent of TiO₂ displayed a rapid decay on CO₂ multi-sorption performance in FBR. Actually, CO₂ sorption using Ca-Al-CO₃ powder has

an obvious drawback, as quickly breakthrough appearance in FBR. In addition, Ca-Al-CO₃ granule became easily fragile material after repeated high-temperature swimming adsorption process. The mechanical strength needs to be improved by using TiO₂ as support. At the same time, this figure indicated a clear co-existence of Ca-Al-CO₃ and TiO₂ in the magnification part. The morphology showed Ca-Al-CO₃ was entirely separated by surrounded TiO₂ that was suspected to as an effective isolator of in Ca-Al-O LDO reactor.

As shown in this figure, XRD patterns demonstrated that specific absorption peaks were observed in calcined Ca/Ti granule, including of anatase (A) and rutile phase (R) of TiO₂, mainly of CaO and CaCO₃ for calcined Ca-Al-CO₃, and CaTiO₃ for granule. Wherein, a commercial product of TiO₂ (Degussa P25) has 80:20 (w/w) of A/R, which is accordance with observed patterns. The hydroxalite-like structure is merely existed at larger than 400°C calcinations [10], thus resulting in the structure change from LDH-like formation of nascent Ca/Al carbonates to calcined Ca-Al-CO₃ with layered double oxide (LDO) structure at 600°C-calcination. Besides, by using TiO₂ as binder, calcination of TiO₂/CaCO₃ to form CaTiO₃/CaO composition was found in the XRD patterns of granule.

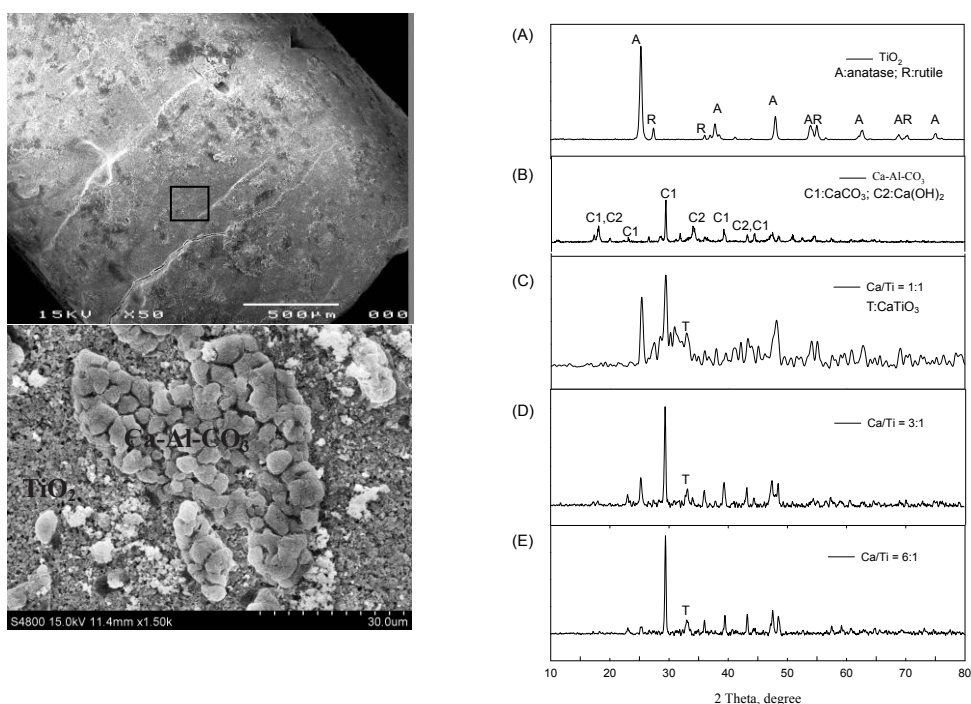


Fig. 3. Left: SEM imagines of Ca/Ti granule. Right: XRD patterns of TiO₂, calcined Ca-Al-CO₃ powder and calcium aluminates granules with molar ratio of Ca:Al of 1:1, 3:1 and 6:1.

3.2 Investigation of CO₂ sorption capacity

Multi-cycle stability was tested using prepared sorbents in TGA. As shown in Fig.4(A), the result showed that calcium acetate derived Ca-Al-CO₃ powder exhibited high CO₂ capacity of about 54 wt% at the first cycle. This material exhibited an improved performance with at least 90% recovery of initial capacity, as shown of approximately 50wt% capacity after 100 cycles (9,000 min). There is a conservative estimation that CO₂ sorption weight is maintained as 50 times of used sorbent weight after 150 hours.

The mixing of Ca-Al-CO₃ (Ca) and TiO₂ (Ti) powder is feasible to prepare granule as CO₂ sorbents. In various ratio of $x=Ca/Ti$, CaO content of sorbent is decreased with increased of TiO₂. Thus as in Fig.4(B), the initial capture weight of these granules was raised with higher Ca content. However, CO₂ sorption weight be became gradual saturation at $x=4-6$. When $x=4$, this sorbent has 90% recovery of initial CO₂ capture weight after 15 cycles, which revealed the better performance than others. These outcomes obviously display the good performance of Ca-Al-CO₃ based oxides as CO₂ solid sorbent at high temperature condition.

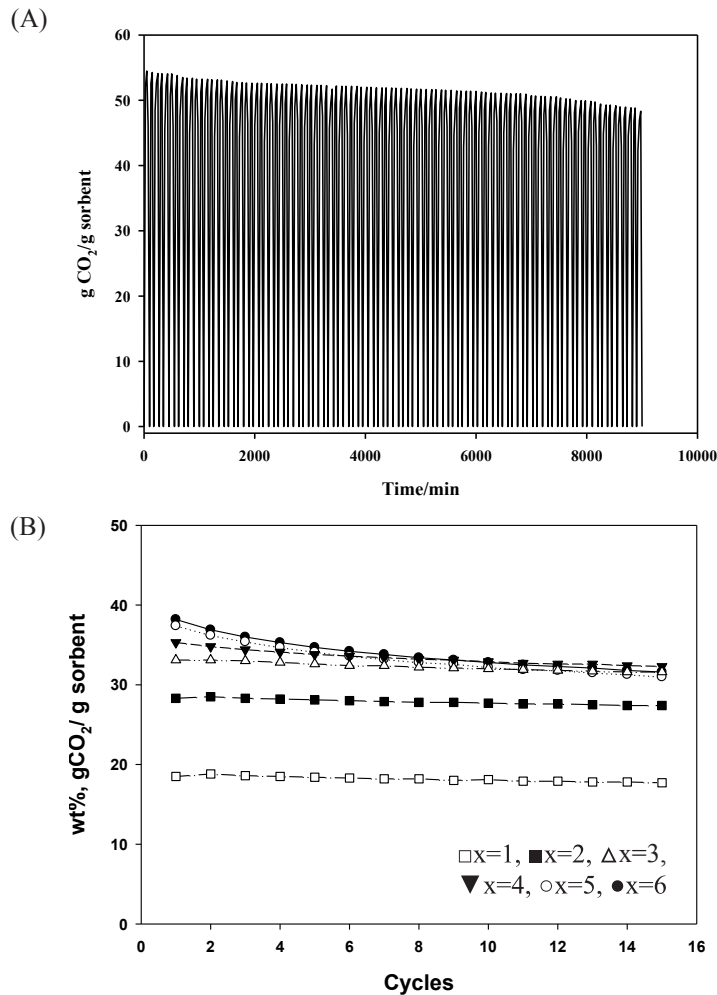


Fig. 4. Testing of CO₂ sorption stability in TGA using (A) Ca-Al-CO₃ powder after 100 cycles and (B) Ca/Ti granules after 15 cycles.

In a fixed-bed reactor, CO₂ sorption stability tested by using Ca-Al-CO₃ powder and Ca/Ti granule ($x=4$) was shown in Fig. 5. The sorption weight was calculated by transform of adsorbing volume into molar volume of ideal gas at 25°C and 1 bar condition. CO₂ sorption performance was estimated by ratio of weight change at n^{th} cycles (W_n) by the first cycle (W_1) using Ca-Al-CO₃ based sorbents. It was found that a fast breakthrough appeared in a short period, emerging CO₂ sorption recovery using pure Ca-Al-CO₃ (powder and granule) was dramatically decayed to 40-50% only after 2-5 cycles and further deteriorated to 33% after 10 cycles. Alternatively, the stability was obviously improved to 80% using granule after 10 cycles. It is believed that TiO₂ provides a binding force to form a matrix of (Ca-Al-CO₃)-Ti-O, effectively separating the Ca-Al-CO₃ segment from local sintering effect on neighboring sorbents in reactor. Therefore, one of the significant drawbacks such as fast breakthrough can be greatly retarded via incorporating TiO₂ into Ca-Al-CO₃. These promising results suggest that granule derived from Ca-Al-CO₃ absorbent may provide outstanding performance in carbonation–calcination processes for CO₂ capture reactor. According to the performance of CO₂ sorption experiment, granule sorbent displays more advantages than powder in FBR.

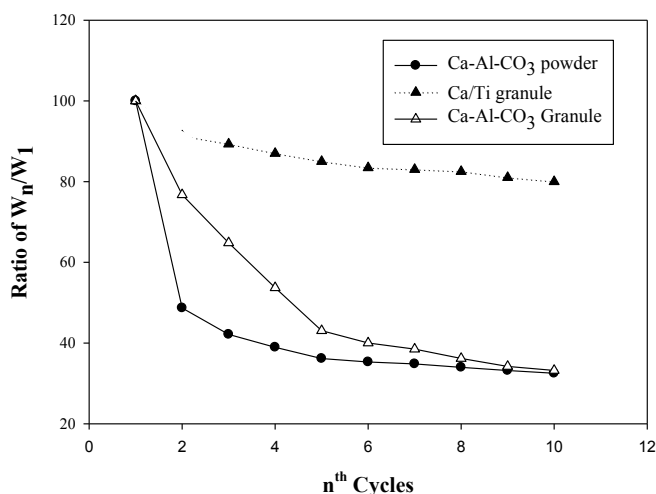


Fig. 5. CO₂ sorption stability using Ca-Al-CO₃ powder, granule and Ca/Ti granule after 10 cycles tested in FBR.

4. Conclusions

In this study, Ca-Al-CO₃ has been used as high-temperature CO₂ sorbent, which is fabricated as powder and Ca/Ti granule. In TGA experiment, relatively high CO₂ capacity of approximately 45~50 wt% after 100 cycles can be achieved with Ca-Al-CO₃ powder; however, CO₂ breakthrough tendency becomes significant, due possibly to the sintering of powder, and results in poor performance for Ca-Al-CO₃ in FBR. The reaction of CO₂ with sorbent is better conducted on granule than over powder, especially at fixed-bed reactor. The results showed that sorption-desorption cyclic test using granule worked successfully at 600-850°C, with 80-90% recovery of initial CO₂ capture weight after 15 cycles in TGA and 70-80% of that after 10 cycles in FBR, respectively. This outcome indicates that CO₂ sorbent developed from calcium aluminates granule with TiO₂ binder is competitive material for controlling CO₂ emission.

Acknowledgements

This work was financially supported by the National Science Council of the Republic of China, Taiwan under Contract No. NSC 101-3113-E-009-003-.

References

- [1] Lisbona P, Marti'nez A, Lara Y, Romeo LM. Integration of carbonate CO₂ capture cycle and coal-fired power plants. A comparative study for different sorbents. *Energy & Fuels* 2010; **24**:728–36.
- [2] Singh R, Ram Reddy MK, Wilson S, Joshi K, Diniz. da Costa JC, Webley PA. High temperature materials for CO₂ capture. *Energy Procedia* 2009; **1**:623-30.
- [3] Florin NH, Harris AT. Reactivity of CaO derived from nano-sized CaCO₃ particles through multiple CO₂ capture-and-release cycles. *Chem Eng Sci* 2009; **64**:187-91.
- [4] Wu SF, Zhu YQ. Behavior of CaTiO₃ /Nano-CaO as a CO₂ Reactive Adsorbent. *Ind. Eng. Chem. Res.* 2010;**49**:2701–06.
- [5] Zhao M, Yang X., Church TL, Harris AT. Novel CaO – SiO₂ Sorbent and Bifunctional Ni/Co – CaO/SiO₂ Complex for Selective H₂ Synthesis from Cellulose. *Environ. Sci. Technol.* 2012; **46**: 2976 – 83.
- [6] Wu CH, Chang YP, Chen SY, Liu DM, Yu CT, Pen BL. Characterization and structure evolution of Ca–Al–CO₃ hydrotalcite film for high temperature CO₂ adsorption. *J Nanosci Nanotech* 2010; **10**(7):4716-20.
- [7] Firas N. Ridha a,b ,Vasilije Manovic a ,Arturo Macchi b ,Edward J.Anthony. High-temperature CO₂ capture cycles for CaO-based pellets with kaolin-based binders. *International Journal of Greenhouse Gas Control* 2012;**6**:164–70.
- [8] Chen H, Zhao C, Yang Y, Zhang P. CO₂ capture and attrition performance of CaO pellets with aluminate cement under pressurized carbonation. *Applied Energy* 2012;**91**:334–40.
- [9] Qin C, Yin J, An H, Liu W, Feng B. Performance of Extruded Particles from Calcium Hydroxide and Cement for CO₂ Capture. *Energy Fuels* 2012; **26**:154 – 61.
- [10] Manovic V, Anthony EJ. Thermal activation of CaO-based sorbent and self-reactivation during CO₂ capture looping cycles. *Environ Sci Tech* 2008; **42** (11):4170-4.
- [11] Yu CT, Wang CH, Hsu MJ, Chyou YP. Development of a novel Ca/Al carbonates for medium-high temperature CO₂ capture, *Energy Procedia*, 2011;**4**:787-94.
- [12] Chang PH, Chang YP, Chen SY, Yu CT and Chyou YP. Ca-Rich Ca–Al-Oxide, High-Temperature-Stable Sorbents Prepared from Hydrotalcite Precursors: Synthesis, Characterization, and CO₂ Capture Capacity. *ChemSusChem* 2011; **4**:1844 – 51.
- [13] Chen Z, Song H. S, Portillo M, Lim CJ, Grace JR, Anthony EJ. Long-term calcination/carbonation cycling and thermal pretreatment for CO₂ capture by limestone and dolomite. *Energy & Fuels* 2009; **23**:1437–44.
- [14] Franco D, Michele L, Massimo S and Juri R. CO₂ Absorption in a Lab-Scale Fixed Solid Bed Reactor: Modelling and Experimental Tests. *Int.J. Thermodynamics* 2004; **7**(3): 123-30.
- [15] Manovic V, Anthony EJ. Sulfation performance of CaO-based pellets supported by calcium aluminate cements designed for high-temperature CO₂ capture. *Energy & Fuels* 2010; **24**:1414-20.