

ENHANCEMENT OF CALCIUM-BASED WASTE FOR CYCLIC CO₂ CAPTURE UNDER SEVERE CALCINATION CONDITION

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Abstract –Calcium looping is a promising approach for CO₂ reduction. A novel synthetic calcium-based sorbents for CO₂ capture were fabricated by integrating calcium looping process and re-utilization of industrial waste. A key advantage of this method is the low cost and reutilization of calcium resource. High alumina cement, carbide slag and by-product of biodiesel were chosen as the calcium precursor, support material and solvent, respectively. The CO₂ capture capacities of synthetic sorbents were examined under the calcination condition of high CO₂ concentration at high temperature, which is closed to the actual atmosphere for industrial applications. The effects of high alumina cement addition on CO₂ capture by the synthetic sorbents were also discussed. Results show that the synthetic sorbent with 90 wt.% CaO achieves the highest CO₂ capture capacity during 10 cycles under calcination condition of 920 °C, 70% CO₂/N₂. After 30 cycles, C-H-90 achieves CO₂ capture capacities of 0.44 and 0.26 g/g under mild (850 °C, 100% N₂) and severe (920 °C, 70% CO₂/N₂) calcination conditions, which are 51.2% and 69.9% higher than those of carbide slag, respectively. X-ray diffraction analysis confirms the existence of two inert minerals, C₇A₁₂ (Ca₁₂Al₁₄O₃₃) and C₂AS (Ca₂Al₂S₂O₇) in the synthetic sorbent, which act as a pore skeleton between CaO particles during cycles stabilizing the porous structure and thus contribute to the impressive CO₂ capture performance of the synthetic sorbent. The proposed synthetic sorbent appears promising for the implement of cost-effective CO₂ capture.

INTRODUCTION

Calcium looping is deemed as one of the most promising technologies for large-scale CO₂ capture due to its low operation cost, high CO₂ uptakes and potential use in sorption enhanced water gas shift (SE-WGS) reaction (Tian et al., 2016, Wang et al., 2015). The calcium looping process is achieved when calcium-based sorbent absorbs CO₂ in a carbonator to form CaCO₃, and the CaCO₃ is then transported into a calciner for the regeneration of CaO and enrichment of CO₂. In this process, the sorbents are expected to undergo repeating cycles of carbonation and regeneration, which makes the long-term CO₂ capture performance become one of the key concerns for industrial applications (Zhang et al., 2016). However, during the repeated cycles of calcination/carbonation, the energy consumption of CaO regeneration from CaCO₃ is provided by the oxy-fuel combustion. Therefore, the CO₂ concentration in the calciner is up to 95%, which implies that the temperature must be maintained over 930 °C to achieve fully decomposition and fast kinetics within short residence time (Duan et al., 2014). Bunch of researches have proved that the presence of CO₂ during calcination may have an adverse effect on the carbonation reactivity of the regenerated CaO and the CO₂ concentration plays a crucial role on the behavior of calcium-based sorbents (Valverde et al., 2014, Valverde and Medina, 2015). The CO₂ uptakes of calcium-based sorbents decay dramatically mainly because of the sintering of CaO particles, leaving an unsatisfactory residue (less than 10%) (Hu et al., 2015).

The use of supports offers a promising way to increase the sintering resistance of calcium-based sorbents. A great portion of works have succeeded in the effective dispersion of stable and inert matrix between active CaO, which avoids the aggregation of CaO grains under high temperature. Refractory materials, such as MgO (Luo et al., 2015a), Al₂O₃ (Broda and Muller, 2012), Y₂O₃ (Zhang et al., 2014), Ca₂SiO₄ (Zhao et al., 2014), MnO₂ (Chen et al., 2011), and some cheaper support materials such as fly ash (Yan et al., 2015a), rice husk ash (Li et al., 2009), bentonite (Manovic and Anthony, 2009), attapulgite (Chen et al., 2013), kaolin (Ridha et al., 2012), and cement (Asiedu-Boateng et al., 2016) have been studied so far. The properties of synthetic sorbents with supports, together with encouraging preliminary results led us to study them in more detail.

Industrial calcium-based wastes as CO₂ sorbents during calcium looping cycles have attracted attention due to low cost and reutilization of calcium resource (Bobicki et al., 2012). Carbide slag (Ca(OH)₂ as the main composition), is a by-product from the hydrolysis process of calcium carbide (CaC₂) for the production of ethylene. At least 900,000 tons of carbide slag is generated from a factory per year in China. Carbide slag has been identified as an industrial solid waste that could not be reutilized. It is interesting to convert it into harmless and useful materials. Our previous works have shown that carbide slag can be used as CO₂ sorbent during calcium looping cycles (Li et al., 2012). Carbide slag is a cheap material that can be also used as a calcium precursor for the preparation of inert material-supported CO₂ sorbent with high activity. The key for the obviously positive effect on CO₂ capture capacity is the uniform mix of carbide slag and inert materials according to the results of our recent study (Ma et al., 2016). It has been proved that sol mixing when at least one of the precursors is soluble powder is easier to well mix than suspension mixing when all precursors are insoluble powder (Liu et al., 2012). Ca(OH)₂ in carbide slag is soluble in glycerol, which can be replaced by the by-product of biodiesel (>90 wt.% glycerol content) obtained from the transesterification process for biodiesel production (Li et al., 2014). About 0.3 kg of glycerol accompanies with each gallon of biodiesel during the transesterification process, which means that billions of glycerol contained in the by-product of biodiesel is produced annually. Thus, the cost for synthesizing sorbents can be further reduced if by-product of biodiesel can be re-utilized in the preparation process of the synthetic sorbent for CO₂ capture.

In this work, a novel synthetic CO₂ sorbent was prepared with carbide slag, high alumina cement and by-product of biodiesel. The by-product of biodiesel as solvent was obtained from the transesterification process for biodiesel production. The synthetic sorbents and raw carbide slag experienced repeating calcination/carbonation cycles in a dual fixed-bed reactor under two different calcination conditions: the mild condition (850 °C, 100% N₂) and the severe condition (920 °C, 70% CO₂/N₂). The mechanism of how cement addition works on calcium-based sorbents was revealed. In addition, the CO₂ capture performance of synthetic sorbents was interpreted in light of detailed morphology and chemical characterizations.

EXPERIMENTAL SECTION

The carbide slag used in this study was obtained from a chlor-alkali plant in Shandong Province, China. The fresh carbide slag was dried overnight at 105 °C, passed through a 0.125 mm sieve and calcined at 800 °C for 10 min prior to the experiments. The chemical components (expressed in the form of oxides) of carbide slag was 69.52 wt% CaO, 0.17 wt% Fe₂O₃, 2.34 wt% SiO₂, 1.52 wt% Al₂O₃, 0.02 wt% MgO, 0.63 wt% others and 25.8% loss on ignition, as determined by X-ray fluorescence. The high alumina cement was supplied by a cement plant in Jinan, Shandong Province, China and its compositions will be discussed in the following section. The by-product of biodiesel was used as the pore-forming agent, which was obtained from the transesterification process of peanut oil and supplied with >90 wt.% of glycerol content (reaction conditions: CaO as catalyst, CaO addition percentage of 6%, reaction temperature of 64 °C, molar ratio of methanol to peanut oil of 12:1 and reaction time of 2h) (Li et al., 2014).

The novel synthetic CO₂ sorbents were fabricated from carbide slag, high alumina cement and the by-product of biodiesel as follows: The calcined carbide slag (2g in total) was put in a glass beaker. 10 mL of deionized water, the weighted amounts of high alumina cement and 200 mL by-product of biodiesel were then added in order under stirring at room temperature. Subsequently, the suspension was stirred at 60 °C for 60 min and then placed in a muffle furnace for combustion at 700 °C under air for 60 min. Then the synthetic CO₂ sorbents were obtained. During the preparation process, the various synthetic CO₂ sorbents containing 90, 80 and 70 wt.% CaO derived from carbide slag were prepared by adjusting the addition of high alumina cement to 60.89, 254, 502.28 mg, respectively. C-H-90, C-H-80 and C-H-70 denote the synthetic CO₂ sorbents with the CaO contents of 90, 80 and 70 wt.%, respectively.

The cyclic CO₂ capture performance of synthetic sorbents was evaluated in a dual fixed-bed reactor including a carbonator and calciner, as shown in Fig. 1. 500 mg of sample was placed in an alumina pan and sent into a calciner at 920 °C under a mixture flow of 70% CO₂/30%N₂ or at 850 °C under one of three options: 100% N₂, 100% H₂O, and 85% H₂O/15% CO₂. The flow was controlled by mass flowmeters with a total amount of 2 L/min. The pan was taken out after 10 min calcination, weighed and sent into carbonator at 700 °C under a mixture flow of 15% CO₂/N₂ or 10% H₂O/15% CO₂/N₂. The sorbent after 20 min carbonation was weighed again. The multiple cycles were operated with the repeating procedures above. The CO₂ capture capacity is defined as the CO₂ adsorption amount per unit mass of the sorbent, as follow.

$$C_N = \frac{m_N - m_{cal,N}}{m_0} \quad (1)$$

where, N is the number of carbonation/calcination cycles. C_N represents the CO_2 capture capacity after N cycles, g/g. m_0 is the initial mass of the sorbent, g. m_N is the mass of the sorbent after the N th carbonation, g. $m_{cal,N}$ is the mass of the sorbent after the N th calcination, g.

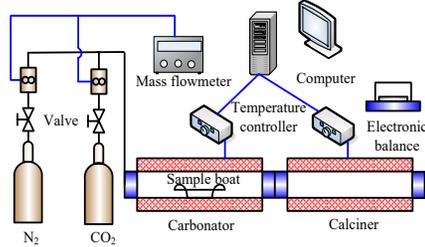


Fig. 1. Diagram of the dual fixed-bed reactor.

The phase compositions of high alumina cement and synthetic sorbents were characterized by X-ray diffraction (XRD, D/Max-III). A field emission scanning electron microscope (SEM, SUPRATM 55) was used to detect the apparent morphology of synthetic CO_2 sorbents and carbide slag before and after cycles.

RESULTS AND DISCUSSION

XRD patterns of the high alumina cement and the various synthetic CO_2 sorbents (C-H-90, C-H-80 and C-H-70) were presented in Fig. 2. The high alumina cement is mainly composed of C_2AS ($\text{Ca}_2\text{Al}_2\text{SiO}_7$) and CA (CaAl_2O_4), with a small amount of CA_2 (CaAl_4O_7) and other impurities that are less than 7 wt.% by quantitative analysis, as shown in Fig. 2(a). It can be noticed that the diffraction peaks distributions are similar among C-H-90, C-H-80 and C-H-70, as illustrated in Fig. 2(b). The diffraction peaks of three synthetic sorbents belong to CaO , C_{12}A_7 ($\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$) and C_2AS , which shows that the new composition, C_{12}A_7 , is formed while C_2AS in the high alumina cement remains stable without chemical changes during the preparation process. There's a large amount of evidence suggesting that the support material, C_{12}A_7 , acts as a skeleton and decreases the aggregation and sintering of adjacent CaO crystallites during the calcination at high temperature (Luo et al., 2015b). Besides, Yan et al. (2015b) confirmed the formation of C_2AS through mechanical mixing of CaO and coal fly ash and found that the dispersed C_2AS was responsible for the high cyclic CO_2 uptake and strong sintering resistance of the synthetic sorbents. Some weak diffraction peaks belonging to $\text{Ca}(\text{OH})_2$ are observed in the synthetic sorbents, which is because a small part of exposed CaO absorbs moisture from the air before the test. Therefore, the conclusion can be drawn that the synthetic sorbents are only made up with CaO and two inert minerals, C_7A_{12} and C_2AS .

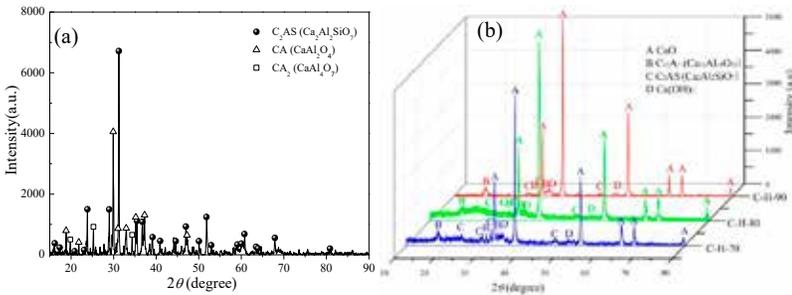


Fig. 2. XRD patterns of (a) high alumina cement and (b) synthetic CO_2 sorbents.

Plots showing the cyclic CO_2 capture capacities of three synthetic sorbents (C-H-90, C-H-80 and C-H-70) are given in Fig. 3. The CO_2 capture performances of the synthetic sorbents and carbide slag are also compared. It is apparent that C-H-90, C-H-80, and C-H-70 exhibit better CO_2 capture performance than

carbide slag. C_{10} of C-H-90, C-H-80, and C-H-70 are 52.86%, 20.95% and 18.10% higher than those of carbide slag, respectively. The lower CO_2 capture capacities of C-H-70 during the previous cycles compared with carbide slag may be attributed to the high alumina cement content, which decreases the active CaO for CO_2 capture in the synthetic sorbents. However, C_N of C-H-70 drops by 49.95% after 10 cycles while C_N of carbide slag drops by 65.91%. It reveals that the addition of high alumina cement enhances the cyclic stabilities of the synthetic sorbents but it may restrain the theoretical maximum CO_2 capture capacity because of the reduced CaO content in the synthetic sorbents. C-H-90 exhibits the highest cyclic CO_2 capture capacity among three synthetic sorbents during 10 cycles. Therefore, further investigation is concentrated on the CO_2 capture performance of C-H-90, as shown in Fig. 4. For the first cycle, C-H-90 exhibits almost the same CO_2 capture capacity with carbide slag, around 0.62 g/g. After 30 cycles, C-H-90 gets residual ones of 0.44 and 0.26 g/g under mild (850 °C, 100% N_2) and severe (920 °C, 70% CO_2/N_2) calcination conditions, which are 51.2% and 69.9% higher than those of carbide slag. The high and stable CO_2 capture behavior of C-H-90 is believed to be attributed to the presence of inert components, C_7A_{12} and C_2AS , which is sufficient to hinder the agglomeration of CaO particles.

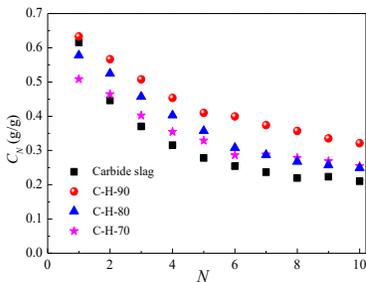


Fig. 3. CO_2 capture performances of synthetic sorbents and carbide slag during 10 cycles (carbonation: 15% CO_2/N_2 , 700 °C and 20 min; calcination: 70% CO_2/N_2 , 920 °C and 10 min).

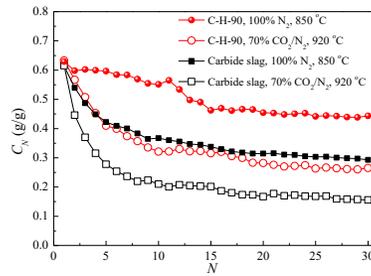


Fig. 4. CO_2 capture performances of C-H-90 and carbide slag in multi-cycle process (carbonation: 15% CO_2/N_2 , 700 °C and 20 min; calcination: 10 min).

CO_2 capture capacities of the synthetic sorbents in the literatures in function of cement content are presented in Fig. 5 and the various test conditions are summarized accordingly in Table 1. It should be noted that all of sorbents reported elsewhere were calcined under mild atmosphere, 100% N_2 . Interestingly, C_N are linearly associated with the cement proportion. C-H-90 in this study shows superior CO_2 capture performance than those in the literature, which means the novel synthetic CO_2 sorbents fabricated from carbide slag, high alumina cement and the by-product of biodiesel is a kind of highly effective CO_2 sorbents.

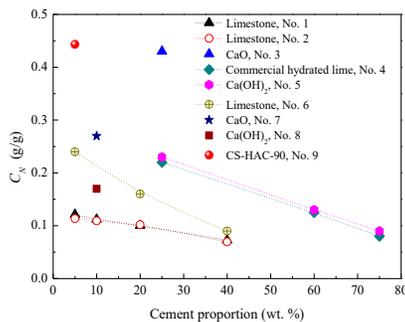


Fig. 5. Summary of CO_2 capture capacities of the synthetic sorbents with addition of cement at the last cycles.

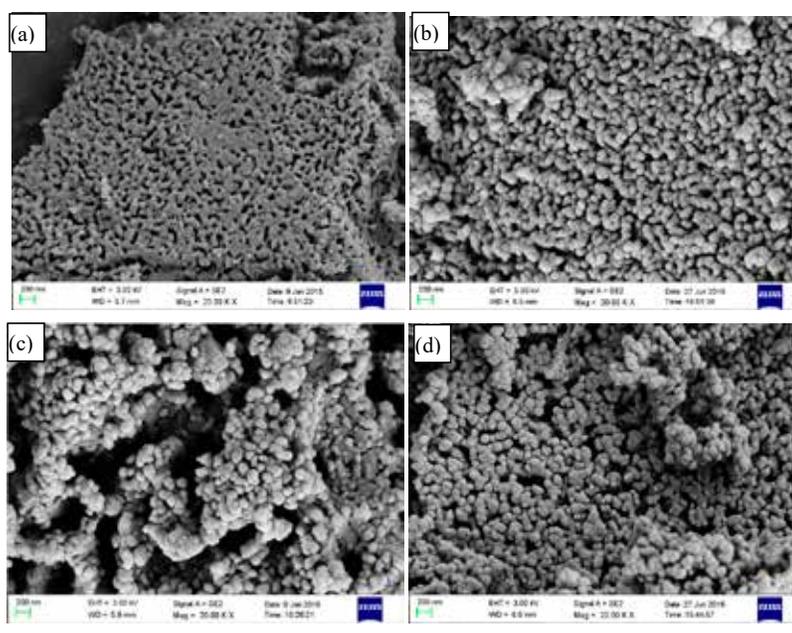
Table 1 Comparison in reaction condition reported in the references involved in Fig. 5.

No.	Ref.	Calcium precursor	Carbonation condition	Calcination condition	Cycle No.
1	(Manovic and Anthony,	Limestone ^a	850 °C, 100%	850 °C, 100%	30

2	2009)	Limestone ^b	CO ₂ , 10 min	N ₂ , 10min	
3	(Luo et al., 2015)	CaO	650 °C, 15% CO ₂ /N ₂ , 15 min	850 °C, 100% N ₂ , 10min	50
4	(Qin et al., 2012)	Commercial hydrated lime	650 °C, 15% CO ₂ /N ₂ , 30 min	900 °C, N ₂ , 30 min	18
5		Ca(OH) ₂			
6	(Sun et al., 2015)	limestone	650 °C, 15% CO ₂ /N ₂ , 30 min	900 °C, 100% N ₂ , 10min	16
7	(Wu et al., 2012)	CaO	800 °C, 25% CO ₂ /N ₂ , 30 min	800 °C, 100% N ₂ , 15 min	90
8		Ca(OH) ₂			120
9	This study	Carbide slag	800 °C, 25% CO ₂ /N ₂ , 30 min	900 °C, 100% N ₂ , 10min	30

Note: Different species of cement were used in ^a and ^b, CA-14 aluminate cement for ^a and secar 51 aluminate cement for ^b.

Fig. 6 shows changes in the morphology of C-H-90 and carbide slag during the cyclic CO₂ capture. The SEM image of the calcined carbide slag presents partial adhesions of CaO particles, while that of initial C-H-90 shows well-defined particles, by comparing Fig. 6(a) and (b). It may be attributed to the release of CO₂ and H₂O during the combustion of by-product of biodiesel that results in these slit pores and gaps between particles in C-H-90. Subsequently, the particles in calcined carbide slag enlarge and numerous large-sized pores are formed after the 10th cycle under the calcination condition of 850 °C and 100% N₂, as shown in Fig. 6(c). Compared to calcined carbide slag, the primary nanosized pores of C-H-90 are present to the large extent in the residue, as shown in Fig. 6(d). It indicates that C-H-90 has higher sintering resistance than carbide slag due to the inert materials of C₇A₁₂ and C₂AS acting as skeleton, which effectively hinders the agglomeration of CaO particles. Compared with Fig. 6(e) and (f), it can be found that severe calcination condition, 920 °C and 70% CO₂/N₂, intensifies the sintering carbide slag, leaving a nonporous and plane surface. However, the morphology of C-H-90 is pretty constant after 10 cycles and shows a slightly grain growth under high temperature. The better pore structure of C-H-90 is beneficial for the effective CO₂ diffusion and more complete carbonation, which may contributes to the much better CO₂ capture performance of C-H-90 than carbide slag.



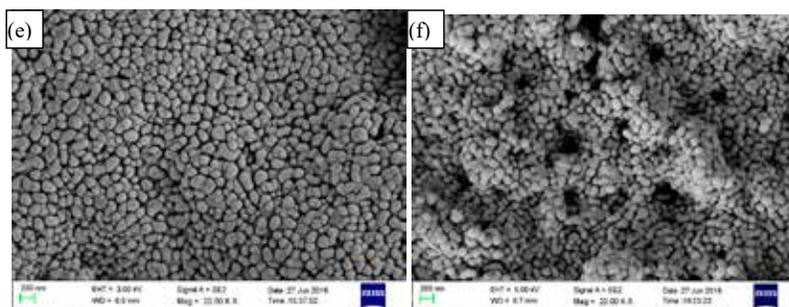


Fig. 6. SEM images of C-H-90 and calcined carbide slag (carbonation: 15% CO₂/N₂, 700 °C and 20 min; calcination: 10 min): calcined raw carbide slag (a); initial C-H-90 (b); calcined carbide slag (c) and C-H-90 (d) after 10 cycles under the calcination condition of 100% N₂, 850 °C; calcined carbide slag (e) and C-H-90 (f) after 10 cycles under the calcination condition of 70% CO₂/N₂, 920 °C.

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