Scientific
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# The Thermogravimeteric Analysis on Carbonation Characteristics of CaO-Based Sorbents

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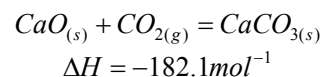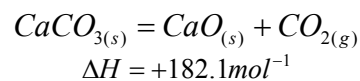    *hdyjin@126.com*

**Abstract:** This study has not only investigated the effect of sorbents kind on the proceed of carbonation by advancing the TGA experiment for three different sorbents including CaCO3, limestone and dolomite, but also examined the loss of limestone activity caused by particle size distribution (80-180 mesh, 180-230 mesh, 230-300 mesh, 300-400 mesh), calcination temperature (750℃, 850℃, 950℃, 1050℃), calcination duration (20min, 60min, 120min) and the $CO_2$ content in calcination gas phase(0%, 15%, 25%, 35%). The TGA experiments results demonstrate that: the strong influence of sorbent selectivity on carbonation conversion rate, specially, dolomite has gained the maximum; the optimum particle size distribution of limestone sample is 230-300 mesh; the loss of particle surface area induced by sorbent particle sintering as a primary element of inhabiting the absorption of $CO_2$ become more pronounced at either higher calcination temperature or longer standing of calcination; and the presence of $CO_2$ in the calcination gas gets forward the particle sintering so as to affecting the performance of sorbent particle at carbonation process.

**Keywords:** Ca-based sorbents; calcination; carbonation;

## 1   Introduction

The climatic deterioration has been introduced by the emission of anthropogenic greenhouse gases, of which 30% is from Fossil fuel combustion plants [1]. One of main practicable option of combating climate change is $CO_2$ capture and storage (CCS), which is more detailed as the produce of the concentrated $CO_2$ steam by the capture of $CO_2$ from flue gas, then employed for liquefaction and storage in underground geological formations and/or in the deep oceans [2-3]. There are three main approaches for capturing $CO_2$ as following: post-combustion separation system, pre-combustion separation system and oxy-fuel combustion, among which, the post-combustion separation process refers to separating $CO_2$ from flue gas in looping cycles by absorption with organic solvents such as monoethanolamine or by solids such as lime[4]. Specifically, CaO-based calcination/carbonation looping cycles is applied in dual fluidized bed system including absorber and regenerator [5]. In this cycle process, $CO_2$ is separated from the combustion gas as $CaCO_3$ is obtained by the carbonation of CaO under the temperature of 600-700℃ ; the sorbent both CaO employed in the adso-

ption process and high concentrations of $CO_2$ are regenerated by calcination of limestone in regenerating reactor at higher temperature., the chemical equations are as follow:

$$CaCO_{3(s)} = CaO_{(s)} + CO_{2(g)}$$
$$\Delta H = +182.1 mol^{-1}$$
$$CaO_{(s)} + CO_{2(g)} = CaCO_{3(s)}$$
$$\Delta H = -182.1 mol^{-1}$$

Thus, the primary criteria, which is applied for optimizing economics of $CO_2$ separation system as well as maintaining the high efficiency, is considered as the capture ability of sorbent. The significant fall of CaO-based sorbent carbonation conversion efficiency is obtained due to different conditions, such as high calciantion temperature, long calciantion duration, high effective $CO_2$ partial pressure and the chemical composition of sorbent, prevailing for CaO sintering during the calcination stage [6-9].

The factors influencing the activity and efficiency of CaO-based sorbent have been extensively studied. The inhibition effect of impurity ($SiO_2$) existed in the sorbent sample as well as the calcination condition such as high calcination temperature and 100% $CO_2$ concentration has been identified by Manovic[10]. Li has conducted

CaO-based sorbent calciantion/carbonation cycle in dual fixed bed to discussing the effect of sorbent kind and particle size distribution on carbonation capacity, and the experimental results show that: dolomite calcined at high temperature has gained higher conversion rate than limestone; the optimal dolomite particle size distribution is about 165-315μm[11]. Fang has found that either limestone or dolomite has obtained the better capturing ability as the particle size distribution is 90-450μm[12]. However, the literatures have not been more than the comprehensive discussion but just focused on some certain factors impacting the sorbent activity and absorption capacity. Thus, the objective of this paper is probing the effect of the sorbent particle size as well as the calcination parameters including calcination temperature, duration and the effective $CO_2$ partial pressure on sorbent activity by thermogravimetry analysis of three different calcium-based sorbent.

## 2    Experimental

### 2.1 calcium-based sorbent

There were three different calcium-based sorbents employed in this study, such as calcium carbonation, limestone and dolomite. The X-ray fluorescence (XRF) elemental analyses of samples investigated are given in Table.1. The three sorbent samples were crushed and sieved to give four particle size distributions, such as 80-160 mesh, 160-230 mesh, 230-300 mesh and 300-400mesh.

**Tab.1 XRF Elemental analyses of CaO-based sorbent samples**

| Component | limestone | dolomite |
|---|---|---|
| CaO/wt % | 50.46 | 34.53 |
| MgO/wt% | 2.87 | 14.64 |
| $Al_2O_3$/wt% | 1.02 | 0.14 |
| $Fe_2O_3$/wt% | 0.33 | 0.09 |
| $K_2O$/wt% | 0.24 | 0.06 |
| $Na_2O$/wt% | <0.10 | <0.20 |
| $SiO_2$/wt% | 3.60 | 0.87 |
| $TiO_2$/wt% | 0.06 | <0.03 |
| $CO_2$/wt% | 41.25 | 49.10 |
| 合计/wt% | 99.92 | 99.66 |

### 2.2 Procedure

Calcination and carbonation of sorbents were carried out with Mettler Toledo Star* TGA/DTA. For each run, about 8 mg of samples was put into basket and rapidly introduced into reactor at desired calcination temperature (750℃, 850℃, 950℃, 1050℃), it is should be noticed that the pure CO2 atmosphere was existed during heating process. The calcination was initiated by a change of flow gas composition (100%$N_2$, 85%$N_2$, 75%$N_2$, 65%$N_2$) , then this step should last 20min in order to complete the calcination. The reactive gas flow rate in TGA apparatus was controlled by flow meter at a flow rate of 50cm$^3$/min. The carbonation of sorbents was set as isothermal conditions at 650 in 15% $CO_2$ ($N_2$ balance) for 20min.

## 3    Results and Discussion

### 3.1 The effect of CaO-based sorbent kind

To investigate the effect of the chemical composition of sorbent on its adsorption behavior, three different Ca-based sorbents, such as calcium carbonation, limestone and dolomite, were employed in this experiment. Meanwhile, the calcination of either sorbent was proceed 20 minutes at 850 ℃in pure nitrogen.

It can be seen in fig.1 that the calcination reaction rate of all sorbent samples were similar as well as the decomposition completed time that is about 2 min. However, it should be noticed that there was some difference exceeded in calcination conversion rate between limestone and dolomite: 90.42% vs 88.46%.

Given the sorbent type employed in the $CO_2$ capture cycle, the carbonation behavior was found significant difference even if the calcium sorbent was calcined under similar condition, especially the carbonation conversion data [13]. Fig.2 confirms this tendency, as it shows that, in case of carbonation process, the maximum of either the initial reaction rate or the conversion data was received only if the dolomite sample was employed; in particular, the carbonation conversion of dolomite was 65.39%, greater than both limestone sample and calcium carbonate sample which were issued about 61.69% and 51.19%. The dolomite generates the calined-sorbent with better pore configuration and this can lead to maximum level of conversion rate owing to the higher content of MgO which is about 14.64%, furthermore, the presence

of the MgO as inactive substance was allowed to restrain the melting of sub-grain as well as the closure of pores, which was also favourable towards promoting the adsorption of $CO_2$ [14]. In addition, there was another parameter given rise to the lower carbonation conversion rate of limestone sample, which is the existence of some impurities such as Fe-, Al- and $SiO_2$. When the sorbent sample was calined, those impurities accumulated in the surface of grains that lead to the decrease of the effective specific surface area [15].
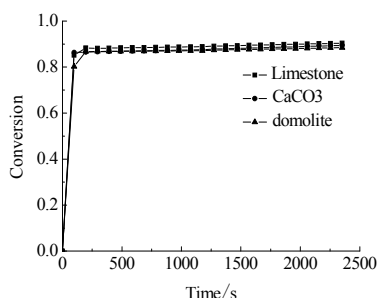


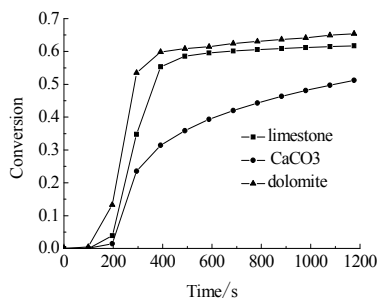**Fig.1 Calcination conversion rates of three Ca-based sorbents**



**Fig.2 Carbonation conversion rate of three Ca-based sorbents**

## 3.2 Effect of particle size distribution

To investigate the possible influence of sorbent particle diameter distribution on the proceed of calcination/carbonation cycle, four particle diameter distributions including 80-180 mesh, 180-230mesh, 230-300mesh and 300-400 mesh of a limestone sample were tested in TGA. And the calcination of either sample was proceeding 20 minutes at 850℃ in pure nitrogen.

The TGA results of four samples were displayed in fig.3 and fig.4. It was can be seen that there was no significant difference of reaction rate and conversion date even if four samples with markedly different particle size distribution was tested in the process of calcination,

expesially the calcination conversions of sorbent samples with 80-180 and that with 180-230 mesh were issued 86.26% and 85.83% respectively; even more important, sorbents with both 230-300 mesh and 300-400 mesh were found the better calcination activity, more specifically, 1.8min and 1.5 min were for complete calcination time, 90.42% and 88.59% for conversion data. This means that in case of the sorbent with smaller particle size distribution employed, the sorbent particle was more readily for both fast-pyrolysis providing the less pore diffusion resistance and the greater specific surface area. However, it was well worth paying attention to that the calcination behavior of sorbent with 300-400 mesh was not better than the sorbent with larger size distribution [16].

It was demonstrated that the carbonation reaction rate of sorbent samples with four different particle size distributions were similar to each other, but there was some difference of carbonation conversion attained which was 55.30%, 56.23%, 61.69% and 58.47% by particle size distribution. This indicated that the calcined-sorbent particle with smaller size distribution was tending to receive the greater effective surface area that was conductive to optimizing the adsorption capacity. However, the conversion was in the trend of decreasing slightly if particle size was less than 48μm. The sintering of sorbent with smaller particle size distribution was intensified by the increases of both $CO_2$ residence time and $CO_2$ diffusion resistance in pores owing to the smaller pore diameter. And the sorbent sintering was considered as the most important factor affacting the carbonation reaction. Furthermore, either the damage of the pore structure or the loss of pore volume arising from the grinding and sieving excessively was regarded as the factor of the decrease of the $CO_2$ adsorption capacity [17].

## 3.3 Effect of calcination temperature

The calcination temperature as an intensive of particle sintering was studied in the range of 750℃ to 1050℃, and the calcination of limestone sample with 230-300 mesh was proceeding 20 minutes in pure nitrogen.

Fig.5 shows there were no appreciable differences

in calcination conversions between the limestone samples tested in different calcination temperature including 750℃, 850℃, 950℃ and 1050℃, the conversions were 88.82%、90.49%、89.18% and 88.40% respectively. Moreover, compared with the curve abtained at, it can be concluded from the TGA result the complete pyrolysis duration was extended about 10 min when calcination was proceeding at 750℃. The results showed that the decomposition rate was sensible to the change of reaction temperature. Thus the calcination was supposed to be carried out at high temperature in order to obtain the stable flux of $CO_2$.

though both calcination rate and sintering rate were enhanced with the increase of the calcination temperature, the sintering rate was more sensible to the higher temperature, thus, with the increase of calcination temperature, the $CO_2$ adsorption capacity decreased owing to smaller specific surface area as was brought by the aggravation of sorbent sintering [18-19].



**Fig.5 Calcination conversion rate of limestone sample calcined at different temperature**



**Fig.3 Calcination conversion rate of different limestone particle size distributions**



**Fig.6 Carbonation conversion rate of limestone sample calcined at different temperature**

### 3.4 Effect of calcination duration

The calcination duration as anther intensive of particle sintering was studied in the range of 20min to 120min, and the calcination of limestone sample with 230-300 mesh was proceeding at 850 ℃ in pure nitrogen.

Fig.7 shows that the complete decomposition times for all samples were about 1.5-2min. This indicated that the increase of the thermal exposure time had no significant effect on the calcination behavior of limestone sample.

It can be seen from Fig.8 that the carbonation conversions were 61.69%, 50.84% and 46.38% when the calcination went on 20 min, 60min and 120min
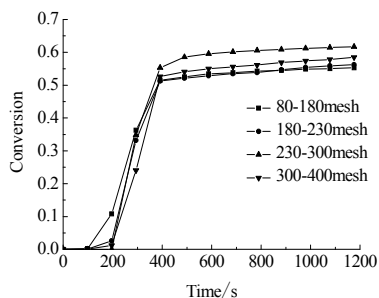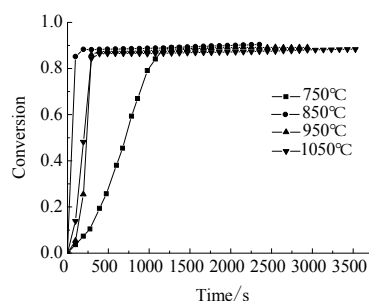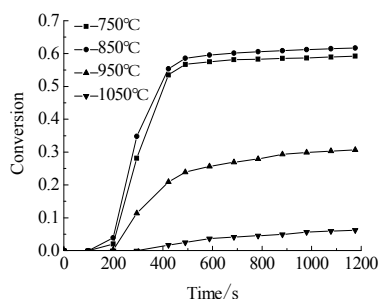


**Fig.4 Carbonation conversion rate of different limestone particle size distributions**

In Fig.6, as can be seen that the $CO_2$ adsorption capacity of sorbent calcined at 850℃ was better than that of sorbent calcined at 750℃, reasons resulting such phenomenon is the minor particle sintering providing by the decrease of $CO_2$ release rate as well as the increase of $CO_2$ residence time at the surface and internal of the particle. However, when the calcination temperature increased to 950℃ even to 1050℃, the carbonation conversion rate dropped to 30.67 % even to 6.23%. Even

respectively. The TGA results demonstrated that the long thermal exposure time of limestone particle led to being lower $CO_2$ capacity as well as the loss of the porosity and surface area resulting from inter-grain melting and the sorbent sintering [20].
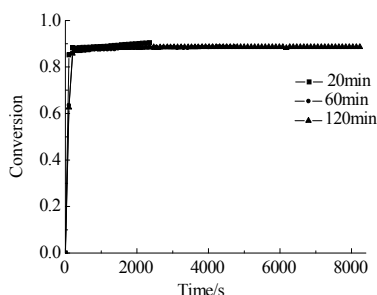


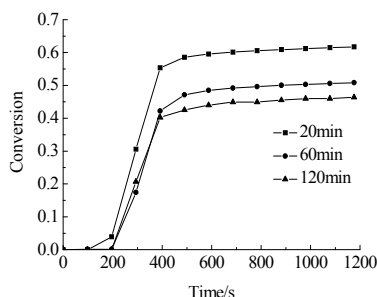**Fig.7 Calcination conversion rate of limestone sample under different calcining time**



**Fig.8 Carbonation conversion rate of limestone sample calcined under different calining time**

### 3.5 Effect of calciantion atmosphere

In calcination, the effective $CO_2$ partial pressure was regarded as one factor of the extent of sorbent sintering that would be govern the activity of sorbent. Thus the calcination atmosphere as an intensive of particle sintering was studied in the range of 65%$N_2$ to 100%$N_2$, and the calcination of limestone sample with 230-300 mesh was proceeding 20 minutes at 850℃.

The experimental results were shown at Fig.9 and Fig.10. The decomposition conversion was similar at different calcination atmosphere, but the reaction rate was lower with the increase of the $CO_2$ content in reaction atmosphere, for example, the complete decomposition time was about 1.8 min if and that prolonged to 10 min if the $CO_2$ ratio was going up to 35%. This suggested that the inhibition of $CO_2$ release

from the internal, surface and boundary of particles could be provided by the higher $CO_2$ partial pressure.

It can be perceived that there is appreciate difference in $CO_2$ capacity between sorbent samples tested at different calcination atmosphere. Especially, the carbonation conversions were 61.69%, 59.91%, 58.29% and 53.47% in order to the increase of $CO_2$ content in calcination atmosphere, from 0% to 35%. In calcination, the increase of $CO_2$ partial pressure existed at the particle surface led to the aggravation of the sorbent sintering that could be given rise to the decrease of particle specific surface area as the index of sorbent adsorption capacity, thus the $CO_2$ adsorption was inhibited in carbonation [21].
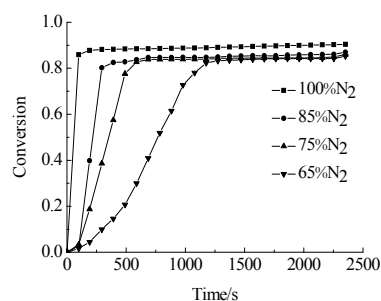


**Fig.9 Calcination conversion rate of limestone sample at different air conditions**
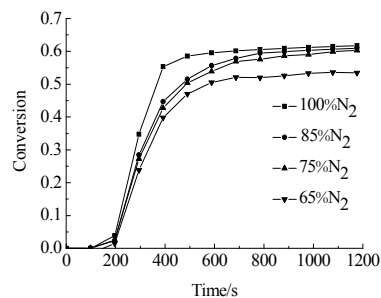


**Fig.10 Carbonation conversion rate of limestone sample calcined under different air conditions**

### 4 Conclusions

Different calcium-sorbent sample can lead to different carbonation patterns and maximum levels of conversions as is the case foe the reaction of calcined-sorbent with $CO_2$, especially the $CO_2$ capacity can get the optimal value in case of dolomite is employed in the cycle; As expected, the limestone

sample with three particle size fractions (80-180mesh, 180-230mesh, 230-300mesh) were tested to show the increase tendency of carbonation conversion as the particle diameters increased, which was caused by increasing resistance to $CO_2$ diffusion towards the free CaO surfaces in the interior of the particle; the fine grinding particle (300-400mesh for this study)had some negligible effect on its capture capacity; the calcination procedure parameters including duration, temperature and atmosphere were regarded as the main factors of the particle sintering degree. The drop of $CO_2$ capture capacity was observed as the reasonable consequence of increasing calcination temperature that led to the particle sintering; moreover, the prolong of calcination duration would get the same results as expect; and carbonation conversion was inhibited caused by the particle sintering which was response to the increase of $CO_2$ partial pressure in clacination atmosphere.

## References

[1] Herzog H，Drakes EM．Carbon dioxide and disposal from large energy system[C]. Annu. Rev. Energy Environ，1996，21：145-166.

[2] Frenud P，Ormerod WG．Profress toward storge of carbon dioxide[J]. Energy Convers. Mgmet.，1997，38：199－204.

[3] Audus H，Freund P. The costs and benefits of mitigation：a full-fuel-cycle examination of technologies for reduction greenhouse gas emmisions[J]. Energy Convers. Mgmet.，1997，38：595－600.

[4] Yang Hongqun，Xu Zhenghe，Fan Maohong, et.al. Progress in carbon dioxide separation and capture：A review[J]. Journal of Environmental Science，2008，20：14－27.

[5] Shimizu T，Hirama T，Hosoda H，et.al. A twin Fluid-Bed reactor for removal of $CO_2$ from combustion processes[J]. Trans IChems，1999，77：62－68.

[6] Borgwardt Robert H . Sintering of nascent calcluim oxide[J]. Chemical Engineering Science，1989，44：53－60.

[7] Vasilije Manovic，Edward J. Anthony，Davor Loncarevic. $CO_2$ looping cycles with CaO-based sorbent pretreated in $CO_2$ at high temperature[J]. Chemical Engineering Science，2009，64：3238－3245.

[8] Fang Fan，Li zhenshan，Cai Ningsheng，Experimental Research and modeling of multiple carbonation/calcination cycle of ca-based $CO_2$ sorbents[J]. Proceeding of the CSEE，2009，64：3238－3245 (in Chinese).

[9] Abanades J.C，Alvarez D. Conversion limits in the reaction of $CO_2$ with lime[J]. Energy &Fuel，2003，17(2)：308－315.

[10] Vasilije Manovic，Jean-pierre Charland，Jone Blamey，et.al. Influence of calcination condition on carrying capacity of CaO-based sorbent in $CO_2$ looping cycles[J]. Fuel，2008，88：1893－1900.

[11] Li Yingjie，Zhao Changsui．Carbonation charateristics in calcium-sorbents cyclic calcination/carbonation reaction process[J]. Proceeding of the CSEE，2008，28(2)：55－60 (in Chinese).

[12] Fang Fan，Li zhenshan，Cai Ningsheng，Effects of Ca-based $CO_2$ sorbents type and particle size on multiple carbonation/calcination cycle[J]. Jounal of Engineering Thermophysics，2008，28(4)：698－702 (in Chinese).

[13] Gemma S. Grasa，J. Carlos Abanades，Monica Alonso，Belen Gonzalez．Reactivity of highly cycled particles of CaO in a carbonation/calcination loop[J]. Chemical Engineering Journal，2008，137：561－567.

[14] Qiao Chunzhen. Study on the $CO_2$ sorbents in the single-step hydrogen production from carbonaceous energy[D]. Beijing：Institute of Engineering Thermophysics，2006(in Chinese).

[15] Stanmore BR，Gilot P. Review – calcination and carbonation of limestone during thermal cycling for $CO_2$ sequestration[J]. Fuel Process Technol，2005，86：1707－1743.

[16] A. Trikkel. Estonian calcareous rocks and oil shale ash as sorbent for $SO_2$[D]. Tallinn Technical University，2001.

[17] Zhicheng Ye，Wuyin Wang,，Qin Zhong，Ingemar Bjerle. High temperature desulfurization using fine sorbent particles under boiler injection conditions[J]. Fuel，1995，74：：743－750.

[18] Borgward R.H. Sintering of nascent calcium oxide[J]. Chem. Eng. Sci.，1989，44(1)：23－60.

[19] Gonzalez G.S，Alonso M，Abanades J.C . Modeling of deactivation of CaO in a carbonate loop at high temperatures of calcination. . Ind. Eng. Chem. Res.，2008，47：9256－9262.

[20] J. Agnew，E. Hampartsoumian，J.M. Jones，W. Nimmo. The simultaneous calcination and dintering of calcium based sorbent under a combustion atmosphere. Fuel，2000，79：1515－1523.

[21] Mai M.C，Edgar T.F. Surface area evolution of calcium hydroxide during Calcination and sintering.. AICHE J，1989，35：30－36.