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Enhancement in cyclic stability of the CO_2 adsorption capacity of CaO-based sorbents by hydration for the calcium looping cycle

Chien-Cheng Li [a,*], Jui-Yen Cheng [a], Wan-Hsia Liu [a], Chin-Ming Huang [a], Heng-Wen Hsu [a], Hong-Ping Lin [b,*]

[a] Green Energy and Environment Research Laboratories, Industrial Technology Research Institute, Hsinchu 31040, Taiwan
[b] Department of Chemistry, National Cheng Kung University, Tainan 70101, Taiwan

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ABSTRACT

In this paper, the reactivation of limestone was effectively enhanced and recovered by steam and/or liquid water hydration processes. The decay rate of the activity in carbonation conversion was improved by the steam hydration of the sorbents during decarbonation/carbonation reactions. The carbonation conversion activity of limestone with a particle size of 1.5 μm remains at 65% with hydration under 2.9 mol% steam after 20 decarbonation/carbonation cycles, while the un-hydrated sorbent shows a lower carbonation conversion of 34%. The activity preservation in the carbonation conversions of three representative particle size ranges of 1.5, 37–74, and 250–500 μm are 30, 14, and 6% after 20 cycles, respectively, with a hydration treatment of 2.9 mol% steam. Pore formation and roughness on the sorbents induced by steam hydration contributed significantly to the enhanced carbonation conversion during the decarbonation/carbonation cycles. The sorbent, with a particle size of approximately 1.5 μm, exhibited higher regeneration and recovery of carbonation conversion. Combined with the liquid water hydration, the carbonation conversion activity of the limestone can recover 80–90% of the original.

1. Introduction

The use of fossil fuels has led to increased atmospheric concentrations of CO_2, a major contributor to the greenhouse effect. It is thus important to reduce anthropogenic emissions of CO_2 when burning such fuels. Several different approaches to separating CO_2 from flue gas streams have been developed [1–6], of which the use of CaO-based sorbents is a promising and cost-effective method for CO_2 capture. With this technique, CaO is carbonated at high temperatures into $CaCO_3$, which is regenerated into CaO upon thermal decarbonation. CO_2 separation from flue gas is a multi-cycle process in a dual reactor, which involves the reaction of CaO with CO_2 from flue gas in the carbonator, and regeneration of sorbent after high-temperature calcination. The cyclic process shows that carbonation is an exothermic reaction, while decarbonation is an endothermic one. The CO_2 capture by CaO sorbent is based on the following reversible chemical reaction (Eqs. (1) and (2)) [1–18]:

$$CaO_{(s)} + CO_{2(g)} \rightarrow CaCO_{3(s)} \quad \Delta H^{\circ}_{298\,K} = -178\ \text{kJ/mol} \tag{1}$$

$$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)} \quad \Delta H^{\circ}_{298\,K} = +178\ \text{kJ/mol} \tag{2}$$

Several studies have demonstrated multiple carbonation/decarbonation reactions of limestone, and indicated that the carbonation capacity decreases with the increasing number of cycles due to sorbent sintering. This is caused by the highly exothermic carbonation process, the increase in volume from CaO to $CaCO_3$, and the lower Tammann temperature of $CaCO_3$ (533 °C) [1–18]. Therefore, it is important to improve the durability of the CaO-based sorbents for use in carbonation/decarbonation cycles.

Hydration has been found to be a useful method for the reactivation of spent limestone-derived sorbent. The molar volumes of $CaCO_3$, CaO and $Ca(OH)_2$ are 36.9 cm^3/mol, 16.9 cm^3/mol and 33.1 cm^3/mol, respectively. A dense nearly impenetrable product layer forms on the surface of particles during carbonation, across which H_2O can penetrate and reactivate the CaO in the inner core (Eqs. (3) and (4)) [1–8,12,13,16,17,19,20]:

$$CaO_{(s)} + H_2O_{(g)} \rightarrow Ca(OH)_{2(s)} \quad \Delta H^{\circ}_{298\,K} = -109\ \text{kJ/mol} \tag{3}$$

$$CaO_{(s)} + H_2O_{(l)} \rightarrow Ca(OH)_{2(s)} \quad \Delta H^{\circ}_{298\,K} = -67\ \text{kJ/mol} \tag{4}$$

The molar volume of $Ca(OH)_2$ is greater than that of CaO, and thus the core expands and particles fracture. This fracturing increases the surface area and porosity of CaO accessible for further reaction upon dehydration [5,7,12,14,19–21].

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* Corresponding authors. Tel.: +886 3 5918637/6 2757575x65342.
E-mail addresses: amd33@ms24.hinet.net, ccli@itri.org.tw (C.-C. Li), hplin@mail.ncku.edu.tw (H.-P. Lin).

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Several studies have investigated the reactivation of limestone-derived sorbents via hydration under different reaction conditions (*e.g.* hydration temperatures, steam pressures, and gas conditions), various types of limestone, different calcination temperatures prior to hydration, and in various apparatuses (*e.g.* thermogravimetric analyser (TGA) and fixed and fluidised bed reactors) [1,6,8–30]. However, few studies have directly explored the effect of particle size on the reactivation by hydration treatment. In this study, we evaluated the effects of particle size and steam and/or liquid water on the decarbonation/carbonation conversions of the CaO-based sorbents over long-term tests. The degrees of the reactivation rate by hydration treatment were also investigated.

2. Experimental

Limestone from Taiwan, with the three different particle size ranges of 1.5, 37–74 and 250–500 μm, was used in all experiments. The chemical composition of the sorbent was determined by inductively coupled plasma mass spectroscopy (ICP-MS) using a Perkin-Elmer Sciex Elan 5000 instrument. The samples were dissolved in HCl, HNO_3, and HF acids for the ICP-MS measurements. The limestone particles were examined using a LEO 1530 field-emission scanning electron microscope (FE-SEM), while X-ray diffraction (XRD) patterns were obtained using a D2 phaser Bruker diffractometer with Cu Kα radiation ($\lambda = 0.1542$ nm) operated at 30 kV and 10 mA. N_2 adsorption–desorption isotherms at 77 K were determined with a Micromeritics Tristar II 3020. Before each measurement, the sample was heated in a vacuum at 120 °C for 2 h. The specific surface area of each sample was calculated according to the BET method, while the pore size distributions were obtained according to the BJH method from the nitrogen adsorption isotherms.

Evaluations of the adsorption capacity and the reactivation of the limestone were carried out by multi-cycle CO_2 capture using a SERARAM SETSYS Evolution thermogravimetric analyzer (TGA) with a SETARAM Wetsys gas humidity generator under atmospheric pressure. The sample holder is a platinum basket 8 mm in diameter and 3 mm in height. For each run in the TGA, around 23 mg of sorbent was introduced into the sample holder. The multi-cycle CO_2 capture experimental measurements were conducted under two decarbonation/carbonation conditions. Each cycle included regeneration under N_2 with and without steam or liquid water, followed by a CO_2 capture step. The CO_2 and N_2 gas flow rate was 100 mL/min.

To investigate the effect of hydration on durability, limestone was calcined at 850 °C under a N_2 atmosphere without and with hydration for 35 min at a heating rate of 40 °C/min. Steam, with the concentrations of 2.9 mol% and 7.8 mol%, was introduced at the temperature range from 650 to 850 °C; after which, the temperature was reduced from 850 to 650 °C under a N_2 atmosphere. Subsequently, the carbonation reactions were carried out at 650 °C in 100% CO_2 for 40 min. For conserving the hydration energy, limestone can also be hydrated at 300 °C under a steam concentration of 7.8 mol% for 5 min. The sample was then reheated to 780 °C for carbonation under a 100% CO_2 atmosphere within 40 min and decarbonation at 960 °C for 35 min. In order to reuse the spent sorbents, a liquid water hydration process was used to regenerate the spent sorbents following each round of 15 decarbonation/carbonation cycles. The spent samples were subjected to liquid water hydration at room temperature for 1 min, dried in an oven at 110 °C for 1 h, and calcined at 960 °C; then, carbonation reactions at 780 °C were repeated. The carbonation conversion (%) was calculated using the following equation [15,18,19]:

$$\text{Carbonation conversion}\,(\%) = \frac{m_n - m_o}{m_o \cdot b} \cdot \frac{W_{\mathrm{CaO}}}{W_{\mathrm{CO_2}}} \times 100 \qquad (5)$$

Table 1
Chemical compositions of natural limestone.

Na	Mg	Al	Si	P	K	Mn	Fe	Ca
ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	%
ND	4202.7	ND	178.3	128.2	2.8	40.5	94.2	10.1

where m_n is the mass of the carbonated sorbent after n cycles, m_o is the mass of the calcined initial sorbent, and b is the content of CaO in the initial calcined sorbent. W_{CaO} and $W_{\mathrm{CO_2}}$ are the mole masses of CaO and CO_2, respectively.

3. Results

The chemical composition of the limestone was determined by ICP-MS, with the Ca content being over 98% (Table 1). Fig. 1 shows the cycle-dependent activities of the limestone for the various particle size distributions with and without steam hydration over 20 cycles of decarbonation/carbonation reactions. During the initial decarbonation/carbonation reactions, the smaller particle size demonstrated higher carbonation conversion. In addition, the carbonation conversion of the sorbent was improved by the 2.9 mol% steam hydration. The 1.5 μm particle size limestone showed the highest performance. In addition, the carbonation–conversion ratio of the 20th cycle to that of the first cycle remained at 65% with steam hydration. The steam hydration during the decarbonation/carbonation reactions can reduce the decay rate of the sorbent. The improvement in the carbonation conversion (*i.e.* difference in the conversion percentage with and without hydration treatment) for the particles with the size ranges of 1.5, 37–74, and 250–500 μm are 30, 14, and 6% after 20 cycles, respectively, via the steam hydration treatment. However, the sorbent with a particle size larger than 250 μm had the lowest improvement in CO_2-capture performance because of its smaller surface area, pore volume, and pore size.

The data of the BET surface areas presented in Table 2 show that the surface area of the spent limestone with steam hydration is greater than that of both natural limestone and spent limestone without steam hydration. Limestone with a larger surface area has better carbonation conversion performance after 20 decarbonation/carbonation cycles, as shown in Fig. 1. These results indicate that the limestone was effectively reactivated by steam hydration. Fig. 2 shows the pore size distributions analyzed by the BJH method of the limestone particles with and without steam hydration after 20 decarbonation/carbonation cycles. In comparison with the initial particles, the spent ones have larger pore sizes

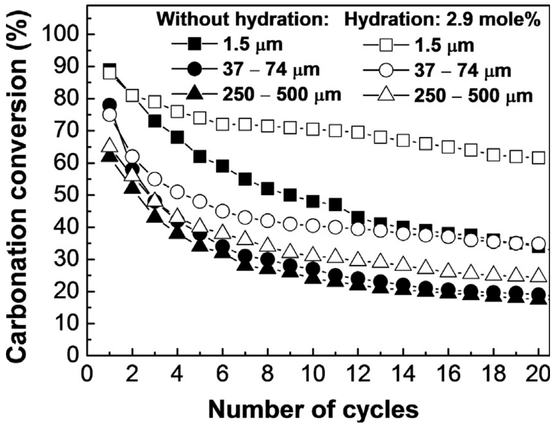

Fig. 1. Carbonation conversions of the limestone particles of various particle size distributions without and with steam hydration during 20 cycles for carbonation at 650 °C and for calcination at 850 °C.