

CO₂ capture by carbonated carbide slag seriflux after drying in calcium looping cycles

He Zirui Li Yingjie Liu Changtian

(School of Energy and Power Engineering, Shandong University, Jinan 250061, China)

Abstract: A new carbide slag (CS) seriflux utilization was proposed. The flue gas from a coal-fired plant was first bubbled into CS seriflux for CO₂ capture. The obtained carbonated carbide slag seriflux (CCSS) was dried and utilized as a CO₂ sorbent in the calcium looping cycles. The CO₂ capture behavior of the dried CCSS and the raw CS was investigated in a dual fixed-bed reactor and a thermo-gravimetric analyzer. The effects of carbonation time, calcination temperature and carbonation temperature on CO₂ capture performance of CCSS in the multiple carbonation/calcination cycles were studied. The results show that the CO₂ capture capacity of CCSS was higher than that of CS. Calcined at 950 °C, CCSS shows better carbonation reactivity than CS, which benefits CO₂ capture under severe calcination conditions. In the range of 700 to 725 °C for the carbonation, CCSS shows the optimal CO₂ capture performance. The calcined CCSS shows better porous microstructure than the calcined CS. The calcined CCSS exhibits a larger surface area and pore volume in the cycles, which favors a higher CO₂ capture capacity in the multiple cycles.

Key words: calcium looping; carbide slag; CO₂ capture

doi: 10.3969/j.issn.1003-7985.2015.02.008

It is widely accepted that the increasing CO₂ concentration in the atmosphere is a significant cause of climate change. In order to mitigate the risk of global warming, a number of technologies have been studied such as solvent scrubbing, oxy-fuel combustion, chemical looping and calcium looping^[1-3]. Calcium looping is based on the reversible reaction between CaO and CO₂ to remove CO₂ from the flue gas of power plants. Ca-based sorbent reacts with CO₂ in a circulating fluidized bed carbonator operated at 600 to 700 °C. The reacted sorbent is then regenerated in another fluidized bed (named calciner), operated at a temperature above 900 °C^[4]. The heat for the regeneration is supplied by oxy-fuel combustion in order to avoid the dilution of the CO₂ stream when fuel is

burned under air atmosphere^[5]. Calcium looping is regarded as a promising technology for CO₂ capture owing to its numerous advantages: the use of cheap and non-toxic sorbents; the relatively small energy penalty imposed on power plants; promising deployment in conjunction with other technologies such as large-scale circulating fluidized beds and cement manufacture^[6-7]. Hence, the calcium looping technology has attracted a great deal of attention^[8-11].

Carbide slag (CS) is a calcium-rich industrial waste, which is the by-product of the hydrolysis reaction of calcium carbide for acetylene gas production. In acetylene gas factories, CS is discharged as seriflux which contains about 92% water. Generally, CS seriflux undergoes a solid-liquid separation process. Then the sediment, which is mostly calcium hydroxide, is utilized in construction and chemical production or buried^[12]. The previous works of our group have proved that the CS can be utilized as a CO₂ sorbent in the calcium looping cycles and achieve a higher CO₂ capture capacity than the limestone^[13]. However, the CO₂ capture capacity of the CS decreases with the number of calcination/carbonation cycles like the natural limestone. Many methods have been proposed to enhance the cyclic CO₂ capture capacity of the calcium-based sorbents. Kierzkowska et al.^[14] synthesized a calcium-based sorbent using Na₂CO₃, (NH₄)₂CO₃ and aqueous solution of NH₃ as a precipitation agent added into the Ca(NO₃)₂ (or Ca(CH₃COO)₂) and Al(NO₃)₃ solution. They found that the CO₂ capture capacity of the synthetic sorbent was 1.8 times as high as that of the limestone after 30 cycles. Florin et al.^[15] prepared a synthetic Ca-based sorbent by bubbling CO₂ through an aqueous solution containing Ca(OH)₂ and Al(NO₃)₃, and its CO₂ capture capacity achieved 2.5 times as high as that of limestone. Gupta et al.^[16] found that a precipitated carbonate calcium prepared by bubbling CO₂ through a slurry of Ca(OH)₂ exhibited a relatively high CO₂ capture capacity in the calcium looping cycles.

In this paper, we propose a precipitation method on the carbide slag seriflux by directly bubbling CO₂ into the seriflux. Then the CCSS was obtained. The CO₂ capture performance of CCSS in the calcination/carbonation cycles was investigated in a thermo-gravimetric analyzer (TGA) and a dual fixed-bed reactor (DFR).

Received 2015-01-02.

Biographies: He Zirui (1990—), male, graduate; Li Yingjie (corresponding author), male, doctor, associate professor, liyj@sdu.edu.cn.

Foundation item: The National Natural Science Foundation of China (No. 51376003).

Citation: He Zirui, Li Yingjie, Liu Changtian. CO₂ capture by carbonated carbide slag seriflux after drying in calcium looping cycles[J]. Journal of Southeast University (English Edition), 2015, 31(2): 204 – 208. [doi: 10.3969/j.issn.1003-7985.2015.02.008]

1 Experimental

1.1 Sample preparation

The CS was sampled from a chlor-alkali plant in Shandong Province, China. The chemical components of the CS were analyzed by X-ray fluorescence (XRF) as shown in Tab. 1. A schematic diagram for the precipitation experiment of the CS seriflux is shown in Fig. 1(a). The wet carbonator contains a porous frit at the bottom providing a good distribution of gas mixture through the seriflux. A

pH probe was used to monitor the variation of pH of the CS seriflux during the carbonation process. In order to model the real CS seriflux, 10 g CS was mixed with 90 g distilled water in a precipitation reactor, and the particles of the CS with the size below 125 μm were chosen. Then, a gas mixture containing 15% CO₂ and 85% N₂ was bubbled into the reactor for the wet CO₂ capture at room temperature until the pH value decreased from 12.6 to 6, which indicated that all the Ca(OH)₂ was converted into CaCO₃. The precipitated product was filtrated and dried in a drying oven at 105 $^{\circ}\text{C}$, and named CCSS.

Tab. 1 Chemical components of CS

w(CaO)	w(MgO)	w(SiO ₂)	w(Fe ₂ O ₃)	w(Al ₂ O ₃)	w(Na ₂ O)	Other	w(LOI)
71.09	0.09	2.51	0.16	1.96	0.02	1.32	22.85

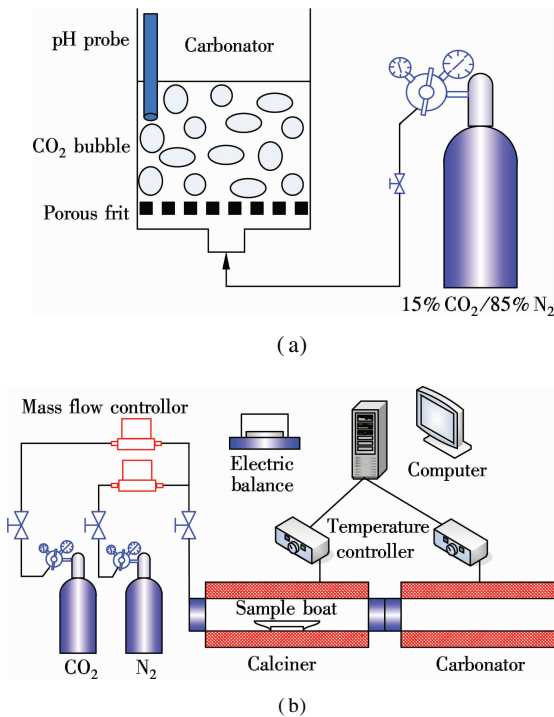


Fig. 1 Schematic diagram of experiment apparatus. (a) The carbonator for precipitation experiment on carbide slag seriflux; (b) Dual fixed-bed reactor for calcination/carbonation cycles

1.2 CO₂ capture in calcination/carbonation cycles

The cyclic calcination/carbonation experiment of the sample for CO₂ capture was performed in a dual fixed-bed reactor (DFR) and a thermo-gravimetric analyzer (TGA) and operated under atmospheric pressure. The DFR contains a carbonator and a calciner as shown in Fig. 1(b). The sample boat loading the sorbent (about 500 mg) can be shifted between two reactors. The calciner was operated at 850 to 950 $^{\circ}\text{C}$ in pure N₂, and the carbonator was operated at 650 to 750 $^{\circ}\text{C}$ in a 15% CO₂/85% N₂ gas mixture. Based on the preliminary experiments, the carbonation time was specified to be 20 min, and the calcination time was 10 min. The calcined sample and its re-carbonated counterpart after each cycle were picked out, stored

and cooled for 2 min in a dry container under N₂. Then the sample was weighted by an electronic balance with a resolution of 0.1 mg. The cyclic carbonation conversion of the sorbent is calculated as

$$X_N = \frac{m_{\text{carb}, N}(t) - m_{\text{cal}, N}}{m_0 b} \frac{W_{\text{CaO}}}{W_{\text{CO}_2}} \quad (1)$$

where t is the carbonation time, s; X_N stands for the carbonation conversion of sorbent at t during the N -th cycle; b is the content of CaO in the initial sorbent, %; $m_{\text{carb}, N}(t)$ represents the mass of carbonated sorbent at t during the N -th cycle, mg; $m_{\text{cal}, N}$ is the mass of sorbent after complete calcination during the N -th cycle, mg; W_{CaO} and W_{CO_2} are the molar mass of CaO and CO₂, respectively, g/mol.

The carbonation kinetics of the CCSS and CS were investigated in a thermo-gravimetric analyzer (TGA). In order to study the cyclic carbonation behavior of the CCSS and CS, the original sorbents and carbonated sorbents (5 ± 0.1 mg) after 9 calcination/carbonation cycles in the DFR were chosen as the samples in the TGA. Therefore, the carbonation behaviors of sorbents were obtained as a function of reaction time during the 1st and the 10th cycles. The furnace temperature of the TGA was increased to a calcination temperature of 850 $^{\circ}\text{C}$ at a heating rate of 30 $^{\circ}\text{C}/\text{min}$, and the sample was held for 15 min under pure N₂. Then, the temperature was dropped to 700 $^{\circ}\text{C}$ for carbonation under pure N₂. At the same time, the reaction atmosphere was switched to 15% CO₂/85% N₂ gas mixture, and the calcined sample was carbonated for 30 min. The carbonation conversions of the sample after the N -th cycle in TGA were calculated by Eq. (1).

1.3 Analysis

The crystalline structure of the sorbents was characterized by a X-ray diffraction (XRD). The calcined CCSS and the CS in the 1st cycle and the 10th cycle were analyzed by the nitrogen adsorption analyzer. The surface area was calculated by the BET method. The pore volume and pore area were computed by the BJH model.

2 Results and Discussion

2.1 Wet carbonation and crystallography of CS and CCSS

Fig. 2(a) shows the XRD spectrum of the CS. It is observed from Fig. 2(a) that the main composition of the CS is $\text{Ca}(\text{OH})_2$, and a little amount of CaCO_3 is also detected. The mixture of 10 g CS and 90 g water is a super-saturated solution of $\text{Ca}(\text{OH})_2$ with the pH value of above 12. When the gas mixture of 15% CO_2 /85% N_2 is bubbled into the slurry, CO_2 dissolves in the water and generates CO_3^{2-} . Then Ca^{2+} is precipitated according to the following reaction^[16]:

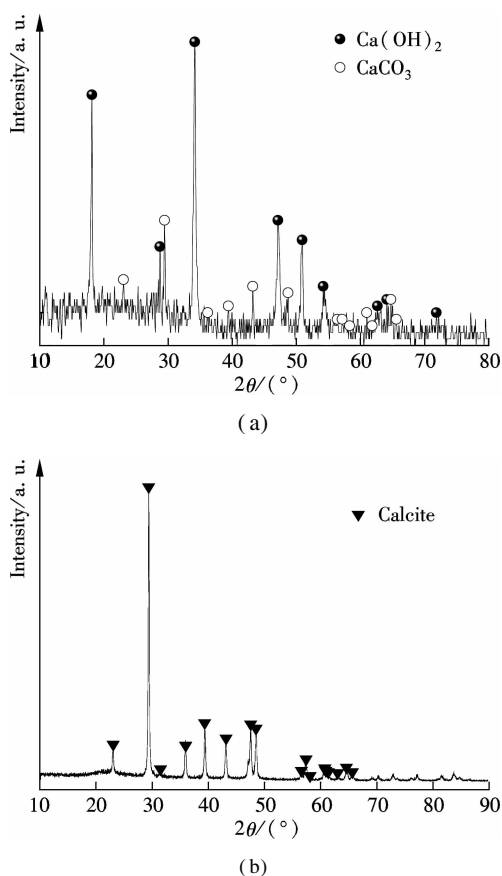


Fig. 2 XRD spectrum. (a) CS; (b) CCSS

The reaction proceeds until the pH value decreases to 6, which indicates that all $\text{Ca}(\text{OH})_2$ in the CS has converted into CaCO_3 . The XRD spectrum of the CCSS is shown in Fig. 2(b). The main composition of the CCSS is CaCO_3 . It should be noted that in this experiment, the precipitated product was not removed in time. As a consequence, CaCO_3 was aged in the high alkaline condition of the precipitating solution.

2.2 Effect of reaction time on CO_2 capture performance of CCSS

The carbonation conversions of the CCSS and CS with

the carbonation time in the 1st and the 10th cycles in the TGA are depicted in Fig. 3(a). It is found that the cyclic carbonation conversion of the CCSS is higher than that of the CS. In the 1st cycle, the carbonation conversions of CCSS at 1 and 30 min achieve 1.3 and 1.1 times as high as those of the CS under the same reaction conditions, respectively. In the 10th cycle, the conversions of the CCSS increase to 1.7 times in 1 min and 1.3 times in 30 min as high as those of the CS, respectively. Fig. 3(b) presents the carbonation rates of the CCSS and CS in the 1st and the 10th cycles in the TGA. It can be seen that the carbonation rate of the CCSS reaches its peak value at 50 s, while the peak value of the CS appears after 100 s. The CCSS exhibits a higher carbonation rate compared with the CS in the initial 100 s in the 1st and the 10th cycles. Although the carbonation conversions and rates of the CCSS and CS decrease with the cycle number, the effect of the number of cycles on the CCSS is less than that on the CS.

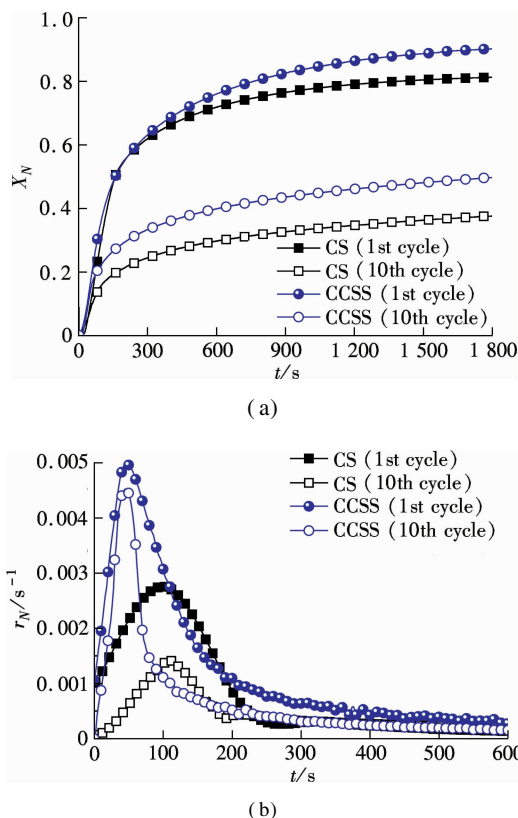


Fig. 3 Carbonation conversions and carbonation rates of CCSS and CS with carbonation time in the 1st and the 10th cycle in TGA. (a) Carbonation conversion; (b) Carbonation rate

2.3 Effect of calcination temperature on CO_2 capture performance of CCSS

Fig. 4 shows the effect of calcination temperature on the cyclic carbonation conversions of the CCSS and CS. With the calcination temperature rising, the carbonation conversions of the CCSS and CS decay significantly with

the number of cycles. The CCSS achieves a higher carbonation conversion than the CS at the same calcination temperature. In addition, the CCSS shows almost the same cyclic carbonation conversion at a calcination temperature of 950 °C with the raw CS calcined at 850 °C. It indicates that CCSS shows better carbonation performance at a high calcination temperature, which favors CO₂ capture by the CCSS under the severe calcination conditions.

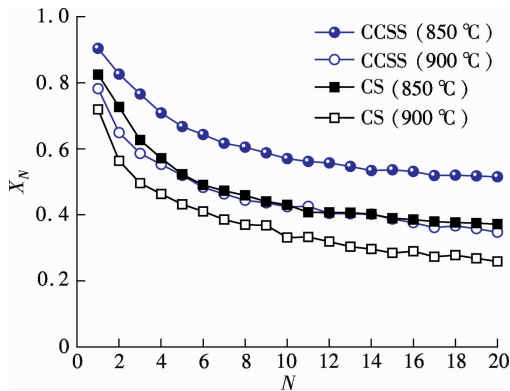


Fig. 4 Effect of calcination temperature on carbonation conversion of CCSS and CS in DFR (10 min calcination in N₂, 20 min carbonation at 700 °C in 15% CO₂/85% N₂)

2.4 Effect of carbonation temperature on CO₂ capture performance of CCSS

Fig. 5 illustrates the cyclic carbonation conversions of the CCSS in the carbonation temperature range of 650 to 750 °C. The carbonation conversion of CCSS increases with the carbonation temperature increasing from 650 to 700 °C. As the temperature increases from 700 to 725 °C, the carbonation conversion of CCSS hardly increases. However, the carbonation conversion decreases as the carbonation temperature increases further. Therefore, the CCSS achieves high CO₂ capture capacity in the carbonation temperature range of 700 to 725 °C.

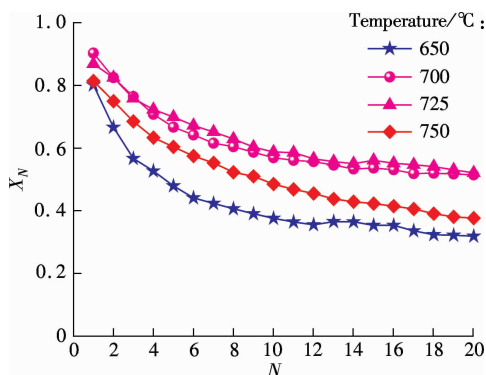


Fig. 5 Effect of carbonation temperature on cyclic carbonation conversion of CCSS in DFR (10 min calcination at 850 °C in N₂, 20 min carbonation in 15% CO₂/85% N₂)

2.5 Microstructure analysis

The surface areas and the pore volumes of the calcined

CCSS and the calcined CS in the 1st and the 10th cycles are presented in Tab.2. After the wet carbonation process, the surface area and the pore volume of the calcined CCSS is higher than those of the calcined CS. The surface area and the pore volume of the calcined CCSS after 1 cycle are 9.92 m²/g and 0.045 cm³/g which are 1.3 and 1.2 times greater than those of the calcined CS for the same number of cycles, respectively. A larger surface area and pore volume favor a higher CO₂ capture capacity of the sorbent. Fig. 6 shows the pore volume distributions of the calcined CCSS and CS in the 1st and the 10th cycles. Compared with the calcined CS, the calcined CCSS shows a higher volume and area of pores in the pore size range of 2 to 10 nm and 30 to 100 nm. The pores in the pore size ranges of 2 to 10 nm and 30 to 100 nm are generated during the calcium ion precipitation in the CS seriflux. In addition, the calcined CCSS maintains more pores in 30 to 100 nm after 10 cycles, compared with the calcined CS. The pores in the range of 30 to 100 nm are important for CO₂ adsorption by the calcium-based sorbent^[2]. Thus, the CCSS exhibits a higher CO₂ capture capacity than the CS.

Tab.2 BET surface areas and pore volumes of calcined sorbents in the 1st and 10th cycles

Samples	Cycle No.	Pore volume/(cm ³ · g ⁻¹)	BET surface area/(m ² · g ⁻¹)
CCSS	1	0.045	9.92
	10	0.031	4.76
CS	1	0.038	7.70
	10	0.023	5.52

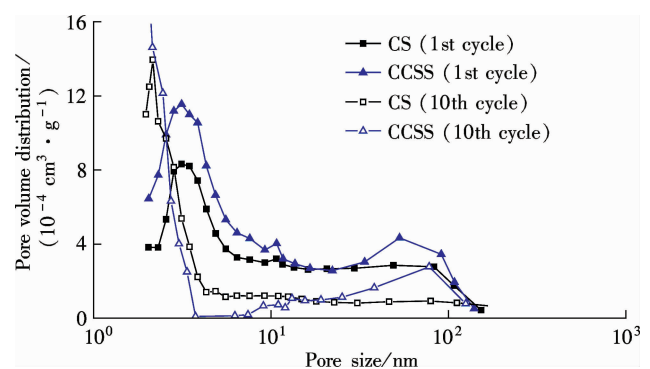


Fig. 6 Pore volume distributions of calcined CCSS and CS in the 1st and 10th cycles (10 min calcination at 850 °C in N₂, 20 min carbonation at 700 °C in 15% CO₂/85% N₂)

3 Conclusion

A wet carbonation process was employed on the CS seriflux, an industrial waste which is discharged as slurry and contains 90% water, by bubbling the gas mixture into it. Then it was dried and utilized as a CO₂ sorbent in the calcium looping. The carbonation behavior of the CCSS in the calcination/carbonation cycles was investigated. Compared with the CS, the CCSS shows a higher

carbonation conversion and rate. The favorable carbonation temperature range of the CCSS is 700 to 725 °C. The CCSS possesses better sintering resistance performance than the CS at the high calcination temperature of 950 °C. The wet carbonation process contributes to the better pore structure of the CCSS in the pore size range of 2 to 10 nm and 30 to 100 nm. The calcined CCSS maintains more pores in 30 to 100 nm than the calcined CS, which is the reason why CCSS exhibits a better CO₂ capture reactivity.

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湿法碳酸化电石渣干燥后在钙循环中的 CO₂ 捕集

何梓睿 李英杰 刘长天

(山东大学能源与动力工程学院, 济南 250061)

摘要:提出一种电石渣资源化利用的新方法. 首先, 将燃煤电站烟气通入电石渣浆液捕集 CO₂. 碳酸化后的电石渣浆液(CCSS)干燥后在钙循环中作为吸收剂捕集 CO₂. 在双固定床反应器和热重仪上研究了 CCSS 和电石渣的 CO₂ 捕集特性, 包括碳酸化时间、煅烧温度和碳酸化温度对 CCSS 循环碳酸化特性的影响. 结果表明 CCSS 的 CO₂ 捕集性能和碳酸化速率均高于电石渣. 煅烧温度为 950 °C 时, CCSS 比电石渣具有更好反应活性, 这有利于在恶劣煅烧条件下捕集 CO₂. 在 700~725 °C, CCSS 表现出了最佳的碳酸化性能. 煅烧 CCSS 比电石渣孔隙结构更好, 具有更大比表面积和比孔容, 这有利于循环捕集 CO₂.

关键词:钙循环; 电石渣; CO₂ 捕集

中图分类号:TK123