



# Article A Study on the Mechanisms of Coal Fly Ash to Improve the CO<sub>2</sub> Capture Efficiency of Calcium-Based Adsorbents

Ziyu Zhao <sup>1</sup>, Kefan Zhang <sup>1</sup>, Jianfeng Luo <sup>2</sup>, Meixuan Wu <sup>3</sup>, Xiyue Wang <sup>1</sup>, Keke Wang <sup>4</sup>,\* and Shengyu Liu <sup>1,\*</sup>

- <sup>1</sup> College of Resources and Environment, Chengdu University of Information Technology, Chengdu 610225, China; zhaozy@cuit.edu.cn (Z.Z.)
- <sup>2</sup> Guiyang Rail Transit Line 3 Construction and Operation Co., Ltd., Guiyang 550081, China
- <sup>3</sup> School of Atmospheric Science, Chengdu University of Information Technology, Chengdu 610225, China
- <sup>4</sup> Sichuan Academy of Eco-Environmental Sciences, Chengdu 610041, China
- \* Correspondence: kekeking2010@163.com (K.W.); lsy@cuit.edu.cn (S.L.)

Abstract: Utilizing calcium-based adsorbents for CO<sub>2</sub> adsorption through cyclic calcination/ carbonization is one of the most cost-effective methods for carbon emission reduction. In order to improve the cycle stability of the adsorbents and the capture efficiency of  $CO_2$ , this study used industrial solid waste coal fly ash for the hydration treatment of calcium-based adsorbent to explore the variations in the cyclic adsorption performance of the adsorbent under different doping ratios and hydration conditions. By means of various characterization techniques, the microscopic mechanism for improving the performance of the modified adsorbent was analyzed from the perspectives of chemical composition, physical structure, and surface functional groups of the adsorbents. The results demonstrated that the modification of coal fly ash could significantly enhance the carbonation performance and cycle stability of the adsorbent in multiple CO<sub>2</sub> capture processes. The modified material doped with 5% coal fly ash had the highest total CO<sub>2</sub> adsorption capacity, which increased by 13.7% compared to before modification. Additionally, the modified material doped with 10% coal fly ash exhibited the strongest cyclic adsorption capacity, which was 14.0% higher than that before modification, and the adsorption attenuation rate decreased by 32.2%. The characterization results showed that the reaction between calcium oxide and coal fly ash formed CaSiO<sub>3</sub> and Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> during the modification process, which was the primary reason for the improvement in the CO<sub>2</sub> capture performance of the modified materials. This study provided a new perspective on the resource utilization of solid waste fly ash and efficient CO<sub>2</sub> capture.

Keywords: adsorbent; coal fly ash; resource utilization; carbon dioxide; carbon emission reduction

# 1. Introduction

With the development of several industries, the global greenhouse effect has been intensifying, and the massive discharge of greenhouse gases such as  $CO_2$  has become the primary cause of global warming [1]. The current resource structure in China, characterized by an abundance of coal, poor oil, and limited gas, has resulted in coal power occupying the largest proportion of China's electricity energy structure for a long time. Against this background, controlling  $CO_2$  emissions from coal-fired power plants is of great significance for the realization of carbon peaking and carbon neutrality goals [2]. Technology utilizing calcium-based adsorbent for cyclic calcination/carbonation to adsorb  $CO_2$  exhibits characteristics such as low adsorbent cost and large adsorption capacity, making it suitable for large-scale industrial applications [3]. The main reaction involves CaO in the adsorbent reacting with  $CO_2$  in the flue gas to produce  $CaCO_3$ .  $CaCO_3$  is then returned to the calcination furnace, where it undergoes high-temperature decomposition to regenerate CaO. This process can enable the cyclic capture of  $CO_2$ , and the high-purity  $CO_2$  obtained by calcination can be reused or mineralized for storage. However, in the process of multiple cycles of calcination and desorption of a natural calcium-based adsorbent, the adsorbent



**Citation:** Zhao, Z.; Zhang, K.; Luo, J.; Wu, M.; Wang, X.; Wang, K.; Liu, S. A Study on the Mechanisms of Coal Fly Ash to Improve the CO<sub>2</sub> Capture Efficiency of Calcium-Based Adsorbents. *Sustainability* **2024**, *16*, 8139. https://doi.org/10.3390/ su16188139

Academic Editor: Adam Smoliński

Received: 6 August 2024 Revised: 8 September 2024 Accepted: 11 September 2024 Published: 18 September 2024



**Copyright:** © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). particles are subjected to prolonged high-temperature conditions for a long time. As their Tammann temperature is significantly lower than the calcination temperature, the particles are prone to sintering, resulting in the fusion of internal grains, which leads to a reduction in the specific surface area of the adsorbent and a substantial decrease in pore volume. The decrease in the active site of the adsorbent inhibits the migration and diffusion of  $CO_{2}$ , ultimately limits its reaction with  $CO_2$ , and significantly reduces the capture efficiency [4,5].

In order to improve the CO<sub>2</sub> adsorption capacity of calcium-based adsorbents derived from solid waste, researchers, both domestically and internationally, have explored various modification methods. CaO-based adsorbent particles loaded with Zr were prepared by the graphite forming method [6], significantly enhancing the cyclic stability and mechanical strength of CaO-based adsorbents. The successful synthesis of Cu/CaO bifunctional materials also effectively inhibited the sintering of CaO during  $CO_2$  desorption [7]. For the Ca-based adsorbent loaded with Mn, the adsorption capacity increased by 75% compared to unmodified material, significantly enriching its pore structure [8]. Utilizing the impregnation-combustion method, the modified CaO-based adsorbent was obtained by doping 15wt% Al<sub>2</sub>O<sub>3</sub> in CaO-based sorbents, which had highly stable adsorption capacity and enhanced compressive strength during the cycle [9]. Additionally, Vruddhi et al. modified CaO by adding nanosheets derived from  $TiB_2$ , which greatly improved CO<sub>2</sub> capture capability and sintering resistance [10]. Research revealed significant variations in the  $CO_2$ trapping performance of adsorbents prepared by different calcium precursors mixed with various Al-containing binders [11]. Zhang et al. added CaO-based particles with aluminum nitrate and oxide as stabilizer precursors [12], achieving a carbonation conversion rate of approximately twice that of pure CaO. Additionally, the use of the extrature-spheronization and cellulose doping modification methods to prepare limestone particles was found to enhance the cyclic  $CO_2$  capture performance of Ca-based adsorbents [13]. Furthermore, the introduction of Zr/Al/Ce metals into the CaO structure resulted in a multi-porous and tiny crystalline structure, which led to a deactivation rate of below 25% [14]. Adjusting the doping ratio of CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>/CaO effectively enhanced structural stability, thereby improving  $CO_2$  adsorption performance [15]. Composite adsorbent, produced by employing mechanical mixing method to load Fe/Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> onto CaO, maintained excellent  $CO_2$  absorption characteristics, even up to 40 reaction cycles with high pressure and temperature [16]. Chen et al. used the co-precipitation method with Ca, Mg, and Zr metals for modification [17], significantly improving the average carbonation conversion rate within ten cycles. Unfortunately, most relevant studies utilized metal doping, which escalated costs and posed challenges for achieving industrial CO<sub>2</sub> emissions reduction.

Studies have demonstrated that modifying calcium-based adsorbents with aluminum compounds and  $SiO_2$  can effectively enhance the carbonation performance of absorbents [9,11,12]. Fly ash was primarily composed of Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>. It can chemically react with CaO, producing substances with large specific surface areas that improve adsorption performance [18,19]. Wang et al. utilized fly ash to directly absorb CO<sub>2</sub>, analyzing its physicochemical properties and mineralization kinetics model [20]. It was found that fly ash contained a small amount of free CaO, yet its performance in CO<sub>2</sub> trapping was limited, presenting a significant challenge as a direct  $CO_2$  adsorbent. Moreover, incorporating fly ash derived from municipal waste incineration as a stabilizer, with added CaO for uniform dispersion, increased the porosity and specific surface area of the adsorbent [18]. The small amount of Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> in BAS reacted with CaO to form Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> and Ca<sub>2</sub>SiO<sub>4</sub>, which mitigated sintering among CaO particles. Notably, the highest CO<sub>2</sub> adsorption rate after 20 cycles occurred at the BAS/CaO ratio of 0.25 [21]. It should be noted that current research predominantly involves organic media combined with fly ash to modify the precursor. However, the use of organic solvents also could increase the cost, which is not conducive to industrial application. Research on the impact of fly ash blending ratios on the adsorption capacity and cycling stability of the adsorbent remains limited.

This study adopted industrial solid waste fly ash from power plants to blend with precursor industrial solid waste limestone. Under deionized water conditions, hydration

modification was conducted to explore the variation rule in adsorbent cyclic adsorption performance under different blending mass ratios and hydration conditions. Simultaneously, the research revealed the intrinsic reasons for the improvement of cyclic adsorption performance from both compositional and microstructural perspectives through characterization methods. This approach achieves waste treatment using waste, which can reduce the costs of industrial treatment and lay the foundation for the further large-scale industrial application of this technology, thereby promoting the development of energy conservation, emission reduction, and carbon neutrality efforts.

#### 2. Materials and Methods

# 2.1. Materials

The fly ash used in the experiment was the fine ash collected from the flue gas of coal-fired power plants. The experimental materials were purchased from Henan Bingrun Casting Materials Co., Ltd. Fly ash was used to modify limestone to improve the cyclic adsorption performance of adsorbents. The chemical compositions of limestone were presented in Table 1, while the chemical compositions of fly ash were listed in Table 2. The content of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> was 45.1% and 24.2%, respectively. The composition of the limestone and ash was derived from the composition report of the experimental drug.

Table 1. Limestone composition analysis (%).

Limestone	CaO	MgO	SiO <sub>2</sub>	Na <sub>2</sub> O	Fe <sub>2</sub> O <sub>3</sub>	$Al_2O_3$	K <sub>2</sub> O	TiO <sub>2</sub>	LOI
Mass fraction	55.16	0.58	0.14	0.03	0.01	< 0.01	< 0.01	< 0.01	43.92

Table 2. Ash composition analysis (%).

Fly Ash	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	SO <sub>3</sub>	TiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	LOI
Mass fraction	45.1	24.2	5.6	2.1	1.21	0.85	0.54	2.8

#### 2.2. Characterization Methods

The surface morphology, atomic species, and content of samples were characterized by a scanning electron microscope energy spectrometer (JSM IT800, JEOL, OXFORD ULTIM Max65, Ltd., Tokyo, Japan) at 15.00 kV acceleration voltage and 8.6 mm working distance. Meanwhile, the surface microstructure of samples was characterized by X-ray Diffraction (XRD, DX-2700BH, Shimadzu Corporation, Tokyo, Japan) at the angle range of 5–80° with a scanning step of 0.02, a scanning rate of  $6^{\circ}$ /min, a voltage of 30 kV, and a current of 20 mA. Additionally, the Accelerated Surface Area and Porosimetry System (SSA-4200, Beijing Biode Electronic Technology Co., Ltd., Beijing, China) were used to measure the specific surface area, pore volume, and pore size distribution of samples. The samples were degassed under a vacuum condition at 200 °C. The mass of the sample after degassing was weighed, and then the samples were placed in liquid nitrogen for adsorption and desorption. Fourier Transform Infrared Spectroscopy (FTIR, Nicolet is 50, Thermo Fisher Scientific Inc., Waltham, MA, USA) was used to characterize the main functional groups on the surface of samples. The light transmittance of the samples was measured in the spectral range of 400–4000 cm<sup>-1</sup> by mixing KBr (Shanghai Aladdin Biochemical Technology Co., Ltd., Shanghai, China) with the samples (100:1) and grinding the tablet.

The first material modification method used was mixing fly ash powder and limestone powder separately in a beaker with varying doping mass ratios of 0%, 1%, 10%, and 20%. The appropriate amount of deionized water was added and stirred at a constant temperature of 50 °C for 3 h using a magnetic stirrer until a suspension was formed. Then, the mixture was taken out and dried in an electric thermostatic drying oven at 85 °C for 8 h. After drying, the samples were uniformly ground and transferred to a tubular furnace. The temperature was raised to 850 °C at 5 °C/min under 100% N<sub>2</sub> atmosphere, maintained at

 $850 \degree$ C for 2 h. After cooling to room temperature, the modified adsorbents were obtained, which were denoted as CaCO<sub>3</sub>/FA (0/5/10/15/20).

In addition, the second modification method involved subjecting the limestone powder to calcination at 850 °C for 2 h and then mixing it with fly ash powder in a beaker according to a specified doping mass ratio. Subsequent steps were performed that were identical to the aforementioned process, resulting in samples labeled as CaO/FA (0/5/10/15/20%).

#### 2.3. CO<sub>2</sub> Capture Reaction Device

Figure 1 depicts a system for a cyclic carbonation reaction device, consisting primarily of a vertical fixed-bed tube furnace and an intelligent temperature control device (XMT-3002C, Nanjing Chaoyang instrument Co., Ltd., Nanjing, China). Experimental gas entered the reaction system via the flow meter from the outlet of the high-pressure gas cylinder. At the outlet, the portable CO<sub>2</sub> detector (B1030, Shenzhen Waset Technology Co., Ltd., Shenzhen, China) was used in the experiment to measure the concentration of  $CO_2$  in real time. During the experimental process, an appropriate amount of adsorbent was first placed in the middle of the vertical fixed-bed tube furnace. N<sub>2</sub> was introduced to purge the air from the furnace. The heating sequence was set to reach 850  $^\circ$ C, and, under the high temperature, carbonation was conducted in an N2 atmosphere. Following thorough calcination, the temperature control program was adjusted to the carbonation temperature. Once the actual temperature of the furnace reached the carbonation temperature, the atmosphere was switched to the carbonation atmosphere for a 1 h reaction period, with real-time recording of  $CO_2$  concentration at the outlet. Subsequently, the carbonation process resumed, and the cyclic carbonation performance experiment was repeated iteratively. The experimental conditions were as follows: carbonation temperature was set to 650 °C, while carbonation atmosphere was 20% CO<sub>2</sub>/80% N<sub>2</sub>. Calcination temperature was set to 850 °C, while the carbonation atmosphere was 100% N<sub>2</sub>.



**Figure 1.** System diagram of fixed-bed reactor. 1—N<sub>2</sub> cylinder; 2—CO<sub>2</sub> cylinder; 3—valve; 4—mass flow meter; 5—intelligent temperature control meter; 6—furnace; 7—thermocouple; and 8—CO<sub>2</sub> detector.

According to the outlet concentration and the mass of the adsorbent, the singlecycle adsorption efficiency was calculated to evaluate the adsorption performance of the adsorbent, as shown in Equation (1). The larger value of x indicated the better adsorption performance of the adsorbent.

$$XN = \frac{P_0 V}{RT_0 n_0} \times 100\% = \frac{10^{-6} P_0 QM}{RT_0 mw} \int_0^t \frac{C_0 - Ct}{1 - Ct} dt \times 100\%$$
(1)

where  $X_N$  is the adsorption rate of the adsorbent (mol/mol%).  $P_0$  is the standard atmospheric pressure ( $P_0 = 101.325$  kPa). *V* represents the actual volume of CO<sub>2</sub> adsorbed by the adsorbent.  $n_0$  is the amount of CaO. *Q* is the inlet mixed gas flow (mL/min). *M* is the relative molecular mass of CaO (56 g/mol). *R* is the molar gas constant (R = 8.314 J/(mol·K<sup>-1</sup>).  $T_0$  is the room temperature (298 K). m is the absorbent filling amount in the fixed bed (g). *w* is the CaO content in the filling adsorbent.  $C_0$  is the initial CO<sub>2</sub> concentration in the mixed reaction gas (mol/mol%).  $C_t$  is the CO<sub>2</sub> concentration in the reactor outlet gas at time *t* (mol/mol%).

### 3. Results and Discussion

# 3.1. Composition and Microstructure Characteristics

The XRD analysis spectra for the calcined products after the first calcination and ten cycles of three adsorbents, CaO/FA (0%), CaO/FA (5%), and CaO/FA (10%), respectively, are depicted in Figure 2. These adsorbents primarily consist of CaO, and extended storage of the products from the initial calcination led to a reaction between CaO and atmospheric H<sub>2</sub>O, resulting in the formation of Ca(OH)<sub>2</sub>. Consequently, partial samples exhibited distinct peaks indicating the presence of both CaO and Ca(OH)<sub>2</sub>. By comparing XRD spectra in the relevant literature, it was found that in Figure 2b,c, in addition to CaO and Ca(OH)<sub>2</sub>, precipitation peaks of CaSiO<sub>3</sub> and Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> also existed [22]. This indicated that alumina and silica in fly ash reacted with calcium oxide to produce CaSiO<sub>3</sub> and Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub>. As physical particle interceptors with high structural hardness, CaSiO<sub>3</sub> and Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> inhibited the sintering phenomenon of the adsorbents and thereby improved the cyclic stability of the calcium-based adsorbents. After undergoing ten cycles of carbonation reactions, there were no significant changes in the material composition, demonstrating great stability.



**Figure 2.** XRD patterns of adsorbents (**a**) CaO/FA0, (**b**) CaO/FA5, and (**c**) CaO/FA10 after the first calcination and 10 cycles.

Figure 3 presents the FTIR spectra of adsorbent materials modified with different doping ratios. Analysis and reference to relevant standard spectra revealed that the characteristic peak at 879 cm<sup>-1</sup> arose from the O-C-O bending vibration of  $CO_3^{2-}$  in incompletely decomposed CaCO<sub>3</sub> during calcination [23]. The characteristic peak at 1470 cm<sup>-1</sup> was attributed to the C-O stretching vibration of  $CO_3^{2-}$  [24]. The broader peak at 3440 cm<sup>-1</sup> was caused by the stretching vibration of -OH in Ca(OH)<sub>2</sub> and bound water [25]. The sharp peak appearing at 3640 cm<sup>-1</sup> was due to the stretching vibration of the Ca/Al-OH bond. Meanwhile, the increase in peaks with the low-frequency range of 500–900 cm<sup>-1</sup> was identified as the symmetric and asymmetric stretching vibrations of -Al-O-Ca and Ca-O bonds [26]. The comparison clearly indicated that after doping, the material exhibited a distinct characteristic peak at 926 cm<sup>-1</sup>, likely attributed to a Si-O-Si stretching vibration [27,28]. According to the FTIR spectroscopy analysis, and combined with the XRD pattern analysis, Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub>, Ca(OH)<sub>2</sub>, CO<sub>3</sub><sup>2-</sup>, SiO<sub>3</sub><sup>2-</sup>, and other substances existed in the modified material.



Figure 3. FTIR spectra of calcined products of adsorbents with different doping ratios.

For adsorbents, the specific surface area and pore size structure of materials were critical indicators reflecting their adsorption performance. Table 3 shows the specific surface area and pore volume of modified adsorbents CaO/FA (5%), CaO/FA (10%), and undoped fly ash-modified CaO/FA (0%) after the first and tenth calcination, respectively. After the tenth calcination of the material, the specific surface area and pore volume of the undoped modified material decreased by 38% and 48%, respectively. Meanwhile, the modified material CaO/FA (5%) and CaO/FA (10%) presented decreases of 17.6% and 15.2% in specific surface area, and the specific pore volume decreased by 40.4% and 42.7%, respectively. These attenuations were significantly lower than those of undoped modified materials. The addition of the modified material resulted in the blockage of some of the pores in the calcium-based adsorbent, a slight decrease in the apparent pore volume, and no significant change to the specific surface area. The experiment results showed that doped fly ash modification conferred adsorbents with enhanced anti-sintering ability at a microscopic level.

Table 3. BET surface area and BJH pore volume of different calcium-based sorbents.

	First Ca	lcination	Tenth Calcination		
Absorbent	$S_{BET}/(m^2/g)$	V <sub>total</sub> /(cm <sup>3</sup> /g)	$S_{BET}/(m^2/g)$	V <sub>total</sub> /(cm <sup>3</sup> /g)	
CaO/FA (0%)	16.379	0.149	10.084	0.077	
CaO/FA (5%)	17.669	0.140	14.551	0.084	
CaO/FA (10%)	16.564	0.136	14.040	0.078	

The scanning electron microscope images before and after 10 cycles of reaction for each modified adsorbent material were depicted in Figure 4, and their surface morphology was analyzed. A comparison between (a) and (b) indicated that CaO/FA (10%) exhibited a higher presence of small particles compared to CaO/FA (0%) prior to the reaction, resulting in a larger specific surface area, which demonstrated that doping fly ash-modified materials effectively enhances the specific surface area of adsorbents. When comparing (a) and (b) with (c) and (d), significant aggregation of small particles into large particles with increased particle size and reduced porosity was observed, indicating sintering of the materials and a substantial reduction in specific surface area after ten reaction cycles. In Figure 4c,d, it is evident that after ten cycles of reaction, the modified material reduced agglomeration and sintering of small particles compared to the unmodified material. Microscopically, it retained a certain porous structure, revealing the formation of a "skeleton-like" structure for modified materials, effectively preventing the collapse of the pore structure. Macroscopically, it is illustrated that the use of fly ash modification could effectively improve the cyclic stability of adsorption materials.



**Figure 4.** Surface morphology of adsorbent CaO/FA0 (**a**) and adsorbent CaO/FA10 (**b**) before reaction and adsorbent CaO/FA0 (**c**) and adsorbent CaO/FA10 (**d**) after 10 cycles of reaction.

### 3.2. Effects of Modification Methods

The carbonation characteristic curves of the modified adsorbents prepared using two different modification methods are presented in Figure 5. It can be seen that the initial carbonation conversion rates of modified adsorbents  $CaCO_3/FA$  (0%) and  $CaCO_3/FA$  (10%), using the first modification method, were 68% and 59%, respectively. The carbonation conversions decreased to 48% and 38% after five cycles, with a decrease in the conversion rates of 20% and 21%, respectively. While the modified adsorbents CaO/FA (0%) and CaO/FA (10%), prepared using the second modification method, exhibited initial carbonation conversions adcreased to 51% and 61%, respectively. After five cycles, the rates of carbonation conversions decreased to 51% and 52%, with conversion rates decreasing by 12% and 9%, respectively. The results indicated that, for materials without fly ash doping, the second modification method slightly reduced their adsorption capacity compared to the first method. However, with an increase in cycle times, the second method effectively

enhanced the anti-sintering performance of the materials. Comparatively, for materials doped with a small amount of fly ash, the second modification method not only increased the adsorption capacity but also significantly improved the anti-sintering performance compared to the first method. The reason lies in the second modification method, where calcium carbonate was calcined to produce calcium oxide, which reacted with water to form calcium hydroxide. Calcium hydroxide further reacted with silica and alumina in fly ash to produce calcium silicate hydrate and calcium aluminate hydrate, which resulted in only a slight reduction in a specific surface area of  $2.52 \text{ m}^2/\text{g}$  after ten cycles, which is significantly less than the  $6.30 \text{ m}^2/\text{g}$  reduction observed in the unmodified materials. It was demonstrated that the modification method effectively increased the specific surface area of the adsorbent. Additionally, the pore volume of the modified material decreased by only  $0.06 \text{ cm}^3/\text{g}$  after ten cycles, while that of the unmodified material was reduced by  $0.07 \text{ cm}^3/\text{g}$ , which indicated the formation of a certain skeleton structure. This structure maintained the pore structure of the adsorbent under high temperatures, preventing collapse and significantly enhancing the cyclic stability of the calcium-based adsorbent [29–31]. Based on this curve, it is predicted that with the increase in cycle times, the CO<sub>2</sub> adsorption capacity of CaCO<sub>3</sub>/FA would decline more rapidly than that of CaO/FA. Therefore, further optimization and improvement of the adsorbent modification methods are warranted to enhance the cyclic adsorption performance, spreading promising application prospects.



**Figure 5.** The change in carbonation conversion rate of undoped (**a**) and doped 10%FA (**b**) modified materials with the time of cycles.

### 3.3. Effect of Doping Ratio

Figure 6 presents the carbonation characteristic curves of modified adsorbents prepared with varying doping ratios of fly ash and limestone. The initial carbonation conversion rates of the five modified adsorbents, including CaO/FA (0%), CaO/FA (5%), CaO/FA (10%), CaO/FA (15%), and CaO/FA (20%) were 64%, 61%, 61%, 58% and 58%, respectively. After ten cycles of reaction, the carbonation conversion rates decreased to 43%, 48%, 49%, 45%, and 43%, respectively (Figure 6b). Furthermore, the non-doping modified CaO/FA (0%) experienced a 33% decline in conversion rate, reducing to 21%, which showed the fastest decay rate. The conversion rates of CaO/FA (5%) and CaO/FA (10%) decreased by 21% and 20%, respectively, reaching 13% and 12%, indicating a significant slowdown in adsorption rate decay. Although adsorbents CaO/FA (15%) and CaO/FA (20%) also exhibited reduced decay rates in adsorption efficiency, the initial conversion rates were lower compared to the unmodified group. It can be concluded that, after ten cycles of adsorption and desorption, the cumulative adsorption capacity of CaO/FA (5%) was the largest, and the adsorption effect was the best. CaO/FA (10%), on the other hand, presented the lowest degree of deactivation and the strongest anti-sintering capability, maintaining a carbonation conversion rate of 49% after ten cycles. After doping with fly ash, the conversion rate of the modified adsorbent on the initial carbonation reaction was lower than that of the unmodified material. The reason was that, during the material production process, the main components SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> in the fly ash reacted with part of calcium hydroxide

to form hydrated calcium silicate and hydrated calcium aluminate, reducing the number of reactants, which led to a significant decline in the conversion rate of  $CO_2$ . Although reaction products such as  $CaTiO_3$ , formed through reactions involving CaO, MgO, and  $TiO_2$ , could enhance the conversion rate of  $CO_2$ , the impact on the conversion rate of the overall reaction was limited due to their low content in the composition. Additionally, other impurities in the composition, including  $SO_3$  and  $Fe_2O_3$ , did not participate in the carbonation reaction process. Therefore, considering this comprehensively, the conversion rate of the first adsorption and desorption reaction was reduced compared to that of unmodified materials [21]. However, the generated products formed a certain skeleton structure within the reactants, making its porous structure resistant to collapse and, therefore, not prone to deactivation, thus enhancing the cyclic stability of the material [29–31].



**Figure 6.** (**a**) Relationship between total carbon dioxide adsorption over ten cycles; (**b**) variation in carbonation conversion rate with FA participants; and (**c**) variation in carbonation conversion rate with time of cycles.

### 4. Conclusions

The modified adsorbent, prepared by hydrating calcium oxide with a certain proportion of fly ash, exhibited significantly higher total CO<sub>2</sub> adsorption capacity than that of the unmodified adsorbent. Among the five groups of modified adsorbents, CaO/FA (5%) material presented the highest total CO<sub>2</sub> adsorption capacity during carbonation, surpassing the unmodified material by 13.7%. After ten cycles of carbonation, CaO/FA (10%) demonstrated the strongest adsorption capacity, with a 14.0% improvement over the unmodified material and a 32.2% reduction in adsorption decay rate. Furthermore, the microporous structure of CaO/FA (10%) was superior to that of CaO/FA (0%) following ten cycles of carbonation, which is consistent with the excellent cyclic carbonation performance of absorbents. During the modified reaction, calcium oxide reacted with the main components of fly ash to form CaSiO<sub>3</sub> and Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub>. CaSiO<sub>3</sub> and Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> acted as physical interceptors between CaO and CaCO<sub>3</sub> particles, serving as a "skeleton" in the modified material that inhibited the sintering phenomenon of the adsorbents, which

significantly improved the regeneration and adsorption capacity of adsorbents. However, excessive doping of fly ash could lead to an accumulation of inert materials that block pores, thereby reducing the adsorption-specific surface area and diminishing cyclic carbonation performance. Therefore, appropriate doping of fly ash could enhance the ability of calcium adsorbents to recycle  $CO_2$ .

Author Contributions: Z.Z.: Methodology, formal analysis, writing—original draft, writing—review and editing. K.Z.: Data collection, writing—original draft. J.L.: formal analysis, methodology. M.W.: Methodology, writing—review and editing. X.W.: Writing—review and editing. K.W.: Writing—review and editing, supervision, methodology. S.L.: Methodology, writing—review and editing, resources. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was supported by the National Natural Scientific Foundation of China (42307525), Talent Introduction Project Foundation, Chengdu University of Information Technology (KYTZ202137), and Open Foundation of Atmospheric Environment Simulation and Pollution Control Key Laboratory (KFKT-YB-202203).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data will be made available on request.

**Conflicts of Interest:** Author Jianfeng Luo was employed by Guiyang Rail Transit Line 3 Construction and Operation Co., Ltd. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

#### References

- 1. Yue, T.; Liu, Q.; Tong, Y.; Gao, J.; Zheng, Y.; Li, G.; Li, R. Analysis of emission evolution and synergistic reduction effect of air pollutants and CO<sub>2</sub> from Chinese coal-fired power plants. *Atmos. Pollut. Res.* **2024**, *15*, 102001. [CrossRef]
- 2. Wang, S.; Wu, J.; Xiang, M.Y.; Wang, S.Y.; Xue, S.X.; Lv, L.H.; Huang, G.H. Multi-objective optimisation model of a low-cost path to peaking carbon dioxide emissions and carbon neutrality in China. *Sci. Total Environ.* **2024**, *912*, 169386. [CrossRef]
- Gao, Z.X.; Li, C.H.; Yuan, Y.N.; Hu, X.D.; Ma, J.J.; Ma, C.H.; Guo, T.; Zhang, J.L.; Guo, Q.J. Utilizing metal oxide enhancement for efficient CO<sub>2</sub> capture and conversion in calcium-based dual-function materials. J. Energy Inst. 2024, 114, 101630. [CrossRef]
- 4. Lin, X.; Zhang, Y.S.; Liu, H.W.; Boczkaj, G.; Cao, Y.J.; Wang, C.Q. Carbon dioxide sequestration by industrial wastes through mineral carbonation: Current status and perspectives. *J. Clean. Prod.* **2024**, *434*, 140258. [CrossRef]
- Imani, M.; Tahmasebpoor, M.; Sanchez-Jim, P.; Valverde, J.; Garcia, V.M. A novel, green, cost-effective and fluidizable SiO<sub>2</sub>decorated calcium-based adsorbent recovered from eggshell waste for the CO<sub>2</sub> capture process. *Sep. Purif. Technol.* 2023, 305, 122523. [CrossRef]
- Long, Y.; Sun, J.; Mo, C.N.; She, X.Y.; Zeng, P.X.; Xia, H.Q.; Zhang, J.B.; Zhou, Z.J.; Nie, X.M.; Zhao, C.W. One-step fabricated Zr-supported, CaO-based pellets via graphite-moulding method for regenerable CO<sub>2</sub> capture. *Sci. Total Environ.* 2022, *851*, 158357. [CrossRef] [PubMed]
- Han, R.; Wang, Y.; Wei, L.F.; Peng, M.K.; Li, Z.Y.; Liu, C.X.; Liu, Q.L. Integrated CO<sub>2</sub> capture and conversion by Cu/CaO dual function materials: Effect of in-situ conversion on the sintering of CaO and its CO<sub>2</sub> capture performance. *Carbon Capture Sci. Technol.* 2024, 12, 100220. [CrossRef]
- 8. Zhang, D.; Zhang, Y.Q.; Lei, P.W.; Yang, Z.Y.; Liu, L.N.; Zhang, Z.K. CaO-based adsorbents derived from municipal solid waste incineration bottom ash for CO<sub>2</sub> capture. *Sustain. Mater. Technol.* **2024**, *39*, e00856. [CrossRef]
- Xu, R.C.; Sun, J.; Zhang, X.Y.; Jiang, L.; Zhou, Z.J.; Zhu, L.; Zhu, J.T.; Tong, X.L.; Zhao, C.W. Strengthening performance of Alstabilized, CaO-based CO<sub>2</sub> sorbent pellets by the combination of impregnated layer solution combustion and graphite-moulding. *Sep. Purif. Technol.* 2023, 315, 123757. [CrossRef]
- 10. Jani, V.; Rasyotra, A.; Gunda, H.; Ghoroi, C.; Jasuja, K. Titanium diboride (TiB<sub>2</sub>) derived nanosheets enhance the CO<sub>2</sub> capturing ability of Calcium Oxide (CaO). *Ceram. Int.* **2022**, *48*, 32380–32388. [CrossRef]
- 11. Wei, S.; Han, R.; Su, Y.; Gao, J.; Qin, Y. Size effect of calcium precursor and binder on CO<sub>2</sub> capture of composite CaO-based pellets. *Energy Procedia* **2019**, *158*, 5073–5078. [CrossRef]
- 12. Zhang, Y.X.; Sun, J.; Jiang, L.; Zhang, X.Y.; Zhao, C.W.; Bu, C.S. Hydrophobic interface-assisted casting of Al-supported, CaO-based sorbent pellets for high-temperature CO<sub>2</sub> capture. *Sep. Purif. Technol.* **2024**, *340*, 126797. [CrossRef]
- 13. Kong, P.J.; Sun, J.; Li, K.K.; Jiang, L.; Sun, R.Y.; Zhang, T.Z.; Zhou, Z.J. Insight into the deactivation mechanism of CaO-based CO<sub>2</sub> sorbent under in-situ coal combustion. *Sep. Purif. Technol.* **2024**, *346*, 127529. [CrossRef]
- Heidari, M.; Tahmasebpoor, M.; Antzaras, A.; Lemonidou, A.A. CO<sub>2</sub> capture and fluidity performance of CaO-based sorbents: Effect of Zr, Al and Ce additives in tri-, bi- and mono-metallic configurations. *Process Saf. Environ. Prot.* 2020, 144, 349–365. [CrossRef]

- 15. Liu, X.; Chen, J.; Ma, Y.; Liu, C.; Huang, A.; He, J.; Wang, M.; Tang, H.; Zuo, W.; Li, Y. Synergistic effects of CeO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> on reactivity of CaO-based sorbents for CO<sub>2</sub> capture. *Sep. Purif. Technol.* **2024**, *347*, 127660. [CrossRef]
- Ma, K.L.; Han, L.; Wu, Y.L.; Rong, N.; Xin, C.J.; Wang, Z.H.; Ding, H.R.; Qi, Z.F. Synthesis of a composite Fe-CaO-based sorbent/catalyst by mechanical mixing for CO<sub>2</sub> capture and H<sub>2</sub> production: An examination on CaO carbonation and tar reforming performance. *J. Energy Inst.* 2023, 109, 101256. [CrossRef]
- 17. Chen, X.B.; Tang, Y.T.; Ke, C.C.; Zhang, C.Y.; Ding, S.C.; Ma, X.Q. CO<sub>2</sub> capture by double metal modified CaO-based sorbents from pyrolysis gases. *Chin. J. Chem. Eng.* **2022**, *43*, 40–49. [CrossRef]
- 18. Zhang, Z.K.; Yang, Z.Y.; Zhang, S.T.; Zhang, D.; Shen, B.X.; Li, Z.C.; Ma, J.; Liu, L.N. Fabrication of robust CaO-based sorbent via entire utilization of MSW incineration bottom ash for CO<sub>2</sub> capture. *Sep. Purif. Technol.* **2023**, 307, 122795. [CrossRef]
- Zheng, Y.Y.; Ge, Z.W.; Sun, H.C.; Wang, L.; Zhang, S.; Lin, X.P.; Chen, Q.C.; Chen, H.S. The role of oxygen vacancy in CaO-Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> materials derived from hydrocalumite for enhanced CO<sub>2</sub> capture cyclic performance. *Chem. Eng. J.* 2024, 481, 147955. [CrossRef]
- Wang, C.L.; Jiang, H.; Miao, E.D.; Wang, Y.J.; Zhang, T.T.; Xiao, Y.Q.; Liu, Z.Y.; Ma, J.; Xiong, Z.; Zhao, Y.C.; et al. Accelerated CO<sub>2</sub> mineralization technology using fly ash as raw material: Recent research advances. *Chem. Eng. J.* 2024, 488, 150676. [CrossRef]
- Jiang, L.; Zhang, Y.X.; Kong, P.J.; Cheng, L.; Liu, G.J.; Sun, J. Coal fly ash-bound limestone-derived sorbent pellets for high-temperature CO<sub>2</sub> capture. *Carbon Capture Sci. Technol.* 2024, 10, 100155. [CrossRef]
- 22. Scaccia, S.; Vanga, G.; Gattia, D.M.; Stendardo, S. Preparation of CaO-based sorbent from coal fly ash cenospheres for calcium looping process. J. Alloys Compd. 2019, 801, 123–129. [CrossRef]
- 23. Liu, J.; Yang, X.Y.; Liu, H.H.; Cheng, W.Y.; Bao, Y.C. Modification of calcium-rich biochar by loading Si/Mn binary oxide after NaOH activation and its adsorption mechanisms for removal of Cu(II) from aqueous solution. *Colloids Surf. A Physicochem. Eng. Asp.* **2020**, *601*, 124960. [CrossRef]
- 24. Wondu, E.; Lule, Z.C.; Kim, J. Polyisocyanate-based water-soluble polyurethane/CaCO<sub>3</sub> composites for gunpowder storage. *Polym. Test.* **2021**, *99*, 107211. [CrossRef]
- 25. Modekwe, H.U.; Moothi, K.; Daramola, M.O.; Mamo, M.A. Corn cob char as catalyst support for developing carbon nanotubes from waste polypropylene plastics: Comparison of activation techniques. *Polymers* **2022**, *14*, 2898. [CrossRef]
- Chang, P.H.; Huang, W.C.; Lee, T.J.; Chang, Y.P.; Chen, S.Y. Self-reactivated mesostructured Ca-Al-O composite for enhanced high-temperature CO<sub>2</sub> capture and carbonation/calcination cycles performance. ACS Appl. Mater. Interfaces 2015, 7, 6172–6179. [CrossRef] [PubMed]
- Lafmejani, M.K.A.; Parsa, A.; Mirmohammadi, M.; Ahmadi, T.; Mirmohammadi, H. A novel and facile synthesis of calcium silicate nanoparticles as a base for root canal cement/sealer under constant potential: Compared to chemical synthesis. *Mater. Chem. Phys.* 2024, 315, 128924. [CrossRef]
- 28. Zhang, L. Surface modification of titanium by hydroxyapatite/CaSiO<sub>3</sub>/chitosan porous bioceramic coating. *Int. J. Electrochem. Sci.* **2020**, *15*, 3616–3626. [CrossRef]
- Chen, H.C.; Khalili, N. Fly-ash-modified calcium-based sorbents tailored to CO<sub>2</sub> capture. *Ind. Eng. Chem. Res.* 2017, 56, 1888–1894.
  [CrossRef]
- Yan, F.; Jiang, J.G.; Zhao, M.; Tian, S.C.; Li, K.M.; Li, T.R. A green and scalable synthesis of highly stable Ca-based sorbents for CO<sub>2</sub> capture. J. Mater. Chem. A 2015, 3, 7966–7973. [CrossRef]
- Yan, F.; Jiang, J.G.; Li, K.M.; Tian, S.C.; Zhao, M.; Chen, X.J. Performance of coal fly ash stabilized, CaO-based sorbents under different carbonation-calcination conditions. ACS Sustain. Chem. Eng. 2015, 3, 2092–2099. [CrossRef]

**Disclaimer/Publisher's Note:** The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.