

Article

Semi-Dry Carbonation Process Using Fly Ash from Solid Refused Fuel Power Plant

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Received: 22 January 2019; Accepted: 8 February 2019; Published: 11 February 2019



Abstract: The increasing CO₂ concentration in the Earth's atmosphere, mainly caused by fossil fuel combustion, has led to concerns about global warming. Carbonation is a technique that can be used as a carbon capture and storage (CCS) technology for CO₂ sequestration. In this study, the utilization of the fly ash from a solid refused fuel (SRF) power plant as a solid sorbent material for CO₂ capture via semi-dry carbonation reaction was evaluated as a simple process to reduce CO₂. The fly ash was exposed to accelerated carbonation conditions at a relative humidity of 25, 50, 75, and 100%, to investigate the effects of humidity on the carbonation kinetics of the fly ash. The reaction conditions such as moisture, concentration of CO₂, and reaction time can affect CO₂ capture performance of fly ash. Due to a short diffusion length of H₂CO₃ in water, the semi-dry process exhibits faster carbonation reaction than the wet process. Especially, the semi-dry process does not require a wastewater treatment plant because it uses a small amount of water. This study may have important implications, illustrating the possibility of replacing the wet process with the semi-dry process.

Keywords: SRF; fly ash; carbon dioxide; carbonation; CO₂ capture

1. Introduction

CO₂ is a main greenhouse gas and undoubtedly a major contributor to global warming. Capturing CO₂ from the atmosphere is an essential parameter of the carbon management for sequestering CO₂ from our environment. The concentration of CO₂ in our atmosphere is promoted by the combustion of fossil fuels for generating electricity [1,2]. In addition, the amount of the fly ash produced from power plants is expected to increase continuously as the demand for electricity increases. Thus, the interest in fly ash utilization has increased [3–6].

Among many CO₂ reduction and sequestration techniques, solid-looping using calcium oxide (CaO) is a promising CO₂ capture process, known as carbonate looping [7–13]. This process is based on the reversible reaction between CaO and CO₂ to form calcium carbonate. The carbonation reaction can be used to remove CO₂ from the atmosphere. Derevschikov et al. prepared a CaO/Y₂O₃ sorbent to capture CO₂ at high temperatures [14]. J. Shi et al. synthesized a CaO/sepiolite sorbent by the hydration reaction [15]. However, these manufacturing processes are complex and uneconomical for industrial application.

Meanwhile, solid refused fuel (SRF), a highly heterogeneous mixture of high calorific fraction of non-hazardous waste materials, has been recognized as a viable alternative to fossil fuels, and is already being used as a fuel in various industrial sectors, including power plants [16]. The fly ash from SRF plants contains about 20 wt% of lime (CaO) which can be used to sequester CO₂ by aqueous carbonation. Thus, studies about utilizing fly ash as a solid sorbent material for CO₂ capture have increased. In the carbonation reaction between CaO and CO₂, water plays an essential role in hydrating the

calcium-based materials to form calcium hydroxide and most studies were conducted in environments with a high amount of water. Loo et al. conducted accelerated wet carbonation experiments on circulating fluidized bed combustion (CFBC) ash (the prepared solution possessed an ash-to-water ratio of 1:10) [17]. Dananjayan et al. and Ebrahimi et al. conducted aqueous carbonation with the water-to-ash ratio of 15:1 with carbonation capacities of 50.3 g and 32 g of CO₂/kg of fly ash, respectively [18,19].

However, although a Ca(OH)₂ aqueous solution can be effectively used as an absorbent to capture CO₂, commercialization of the CO₂ capture process is still hindered because of the high amount of energy required to evaporate water. Moreover, the process needs a wastewater treatment plant which can be a source of greenhouse gasses.

In this study, we investigated the utilization of fly ash as a solid sorbent material for CO₂ capture via semi-dry carbonation reaction. The effects of the amount of moisture, CO₂ concentration, and reaction time on the performance of fly ash was investigated. The rest of the paper is structured as follows: Section 2 describes the experimental framework used to evaluate the semi-dry carbonation. Section 3 contains the composition changes after the carbonation of SRF ash. Sections 4 and 5 present our discussions and conclusions.

2. Materials and Methods

2.1. Materials

Fly ash obtained from Korea District Heating Corporation in Korea was used for this research. The fly ash was dried in an oven at 100 °C for 10 h to remove moisture.

2.2. Semi-Dry Carbonation Reactor

CO₂ capture was conducted in a round-bottom flask with a single neck as shown in Figure 1. The mixture of fly ash (200 g) and water was delivered into the flask. The rotation speed of the flask was fixed at 40 RPM to shake the mixture. The CO₂ stream (99.99%) and N₂ stream (99.99%) were flowed into the reactor using the regulator and the flow meter to control the CO₂ concentration. The total flow rate of the mixture gas was 10 L min⁻¹. The temperature in the reactor was maintained at 25 °C. The flow chart of the experimental method of semi-dry carbonation is shown in Figure 2.

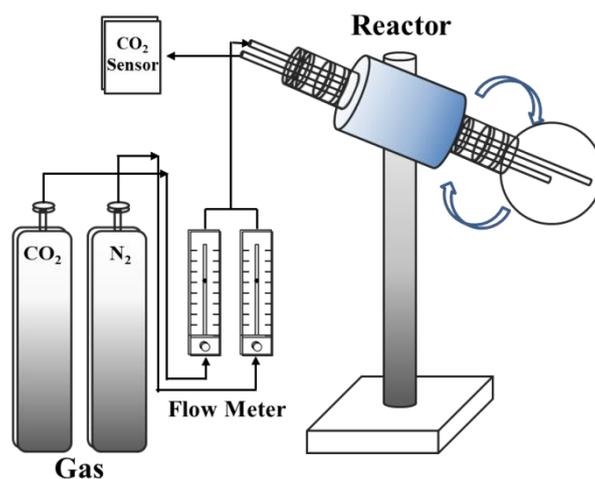


Figure 1. Schematic diagram of the semi-dry carbonation system for the CO₂ capture.

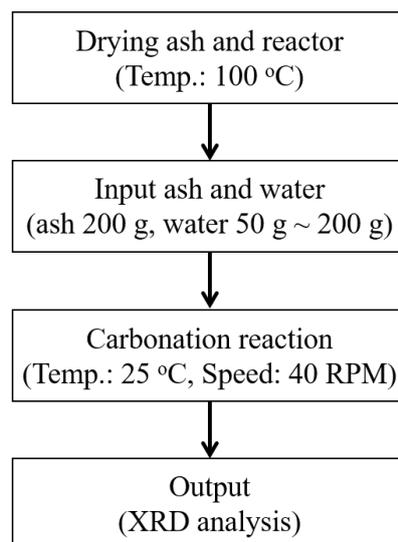


Figure 2. Experimental method of semi-dry carbonation.

2.3. Characterizations

The morphologies and structures of the fly ash were analyzed by SEM (JSM-6700F, JEOL, Tokyo, Japan). The crystal structures were investigated by XRD (X'pert³ Powder, Malvern PANalytical) with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) at the Ssangyong Cement Co. (Daejeon). The particle size was measured using a laser diffraction particle size analyzer (PSA) (Mastersizer S Ver. 2.15, Malvern Instruments, Malvern, UK). The elemental compositions of the fly ash were investigated using X-ray fluorescence analysis (XRF, Primus2, Rigaku, Japan).

3. Results

When SRF is burned in a bottom boiler, most of the unburned material is caught in the flue gas and captured as fly ash. Bottom ash is an incombustible byproduct that is collected from the bottom of the furnaces that burn SRF for generating steam. Therefore, fly ash and bottom ash are quite different physically and chemically. The fly ash and the bottom ash used in the study are shown in Figure 3.



Figure 3. Photographs of (a) fly ash and (b) bottom ash.

The fly ash was composed of fine particles, while the bottom ash was coarse and granular. The color of the bottom ash was dark, dull brown while the color of the fly ash was light brown. Figure 4 shows the morphologies of the fly ash and the bottom ash. The microstructure of the bottom ash (Figure 4b) had a much larger particle size compared to fly ash, which was about the size of sand

but was more porous. As shown in Figure 5, the particle size of the fly ash was between 2 and 130 μm , with D50 (medium diameter) of 25 μm , D10 of 7 μm and D90 of 160 μm .

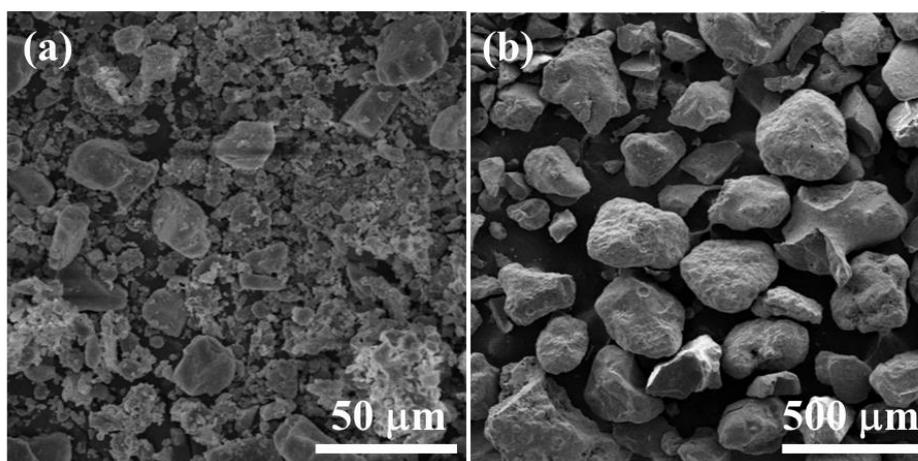


Figure 4. Morphologies of the (a) fly ash and (b) bottom ash.

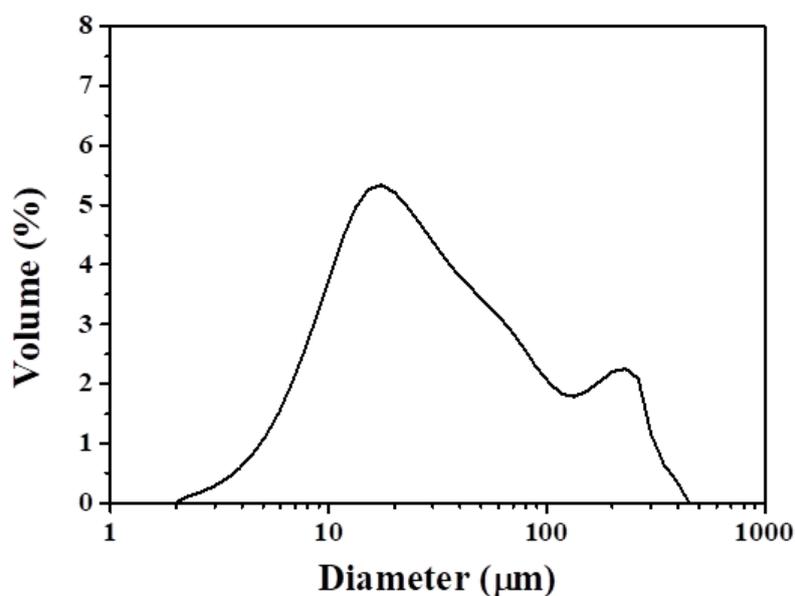


Figure 5. Particle size distribution of fly ash.

Table 1 shows the results of X-ray fluorescence analysis of the fly ash and bottom ash. Concentration of the major elements in the fly ash was given in the form of oxides by XRF. The chemical compositions of the fly ash showed that SiO_2 , Al_2O_3 , Fe_2O_3 , CaO , and Na_2O were the main oxides. On the other hand, the major chemical composition of the bottom ash was SiO_2 . Lead and copper were the most common heavy metals in both ashes (Table 2).

Table 1. Oxide compositions in fly ash and bottom ash (wt%).

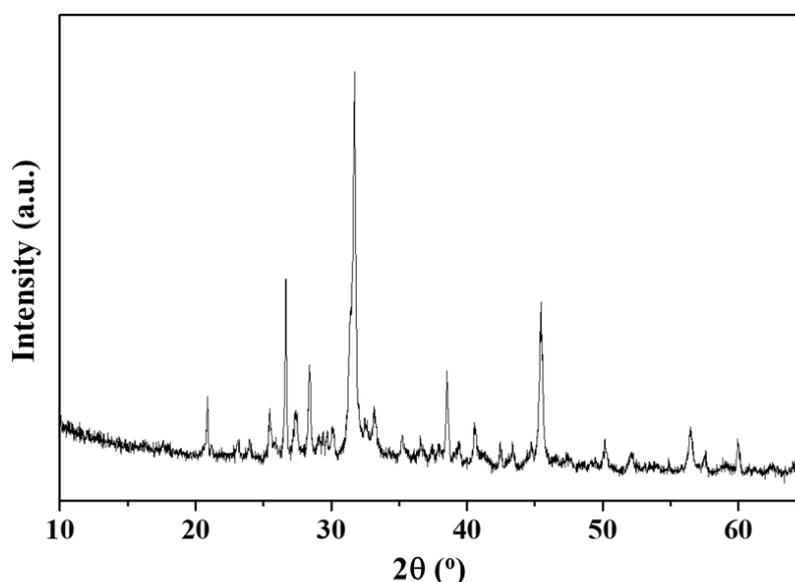
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	N_2O	K_2O	SO_3	P_2O_5	Cl
Fly Ash	24.9	13.2	2.56	17.1	1.82	13.1	2.36	1.29	2.96	12.8
Bottom Ash	85.0	2.90	0.87	7.27	0.50	1.01	0.35	0.18	0.94	0.2

Table 2. Heavy metals in fly ash and bottom ash (mg kg⁻¹).

	Pb	Cd	As	Hg	Cu
Fly Ash	785	33	N.D.	N.D.	5620
Bottom Ash	74	N.D.	N.D.	N.D.	2240

The content of CaO (17.1%) in the fly ash was much higher than that in the bottom ash (7.27%). Therefore, the fly ash, which has high calcium-based contents, was selected for CO₂ capture.

Figure 6 shows the crystal structure of the fly ash. The XRD pattern in Figure 6 confirms the formation of composite powders with mixed crystal structures consisting of periclase (MgO), lime (CaO), calcite (CaCO₃), anhydrite (CaSO₄), quartz (SiO₂), mullite (3Al₂O₃-2SiO₂), hematite (Fe₂O₃), gehlenite (Ca₂Al[AlSiO₇]), halite (NaCl), and sylvite (KCl). The calcium-based materials such as calcite, anhydrite, and gehlenite could be prepared by a high temperature combustion. By using the relative intensity ratio (RIR) technique from the XRD we found that the weight percentage of the periclase, lime, calcite, anhydrite, quartz, mullite, hematite, gehlenite, halite, and sylvite were 0.89, 0.40, 3.02, 7.57, 12.78, 0.54, 2.27, 24.58, 42.46, and 5.48%, respectively (Table 3).

**Figure 6.** X-ray diffraction pattern of fly ash.**Table 3.** Quantitative analytical results obtained by relative intensity ratio (RIR) method (wt%) of the fly ash.

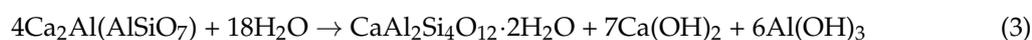
Periclase	Lime	Calcite	Anhydrite	Quartz	Mullite	Hematite	Gehlenite	Halite	Sylvite
0.89	0.40	3.02	7.57	12.78	0.54	2.27	24.58	42.46	5.48

Among the above materials, calcium-based materials (lime, anhydrite, and gehlenite) can react with CO₂:

Lime [20]:



Gehlenite [21]:



To investigate the effect of the amount of moisture on the performance of fly ash for CO₂ capture, reaction with CO₂ was conducted with the following amounts of water: 25 (25-W/A), 50 (50-W/A), 75 (75-W/A), and 100% (100-W/A). The CO₂ concentration and reaction time were fixed at 100% and 60 min, respectively.

Figure 7 and Table 4 show the crystal structure of the fly ash after CO₂ capture using different amounts of moisture and materials by using the relative intensity ratio (RIR) technique from the XRD. The CaCO₃ components of the 25-W/A, 50-W/A, 75-W/A, and 100-W/A were 14.13, 21.31, 26.16, and 21.98%, respectively. The amount of CaCO₃ increased with increasing the amount of water. This suggests that the presence of water played an essential role in hydrating the calcium-based materials to form calcium hydroxide, which then sequestered carbon by forming calcium carbonate. Notably, the amount of CaCO₃ increased from 3.02 to 26.16% when the ratio of the ash-to-water was 1:0.75. The results showed that fly ash of 100 g from a SRF fired power plant captured CO₂ of 10.17 g. However, when the ratio of the ash-to-water was 1:1, the amount of CaCO₃ decreased. CO₂ in gaseous phase does not react with calcium-based materials; it has to dissolve in the water first to form carbonic acid (H₂CO₃) [22]. As shown in Figure 8, the diffusion length of the H₂CO₃ from the outside of the water to the calcium-based materials increased with the increasing amount of water. Therefore, the fly ash with too much water reacted slowly with CO₂.

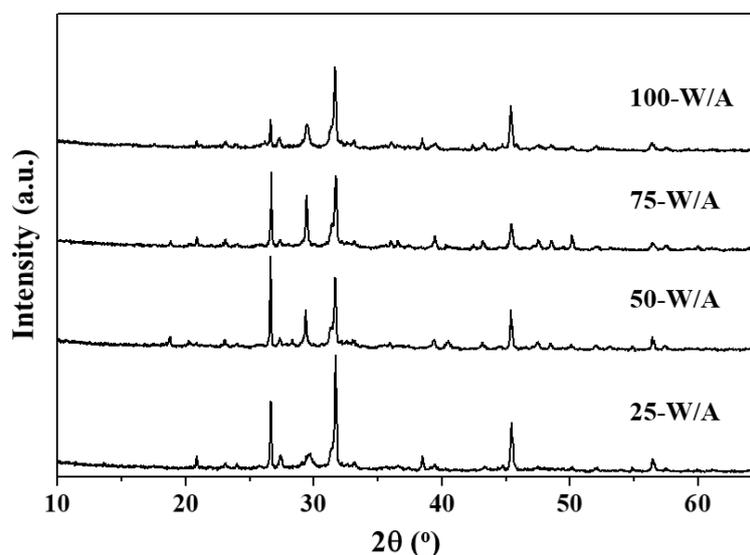


Figure 7. X-ray diffraction patterns of fly ashes after carbonation with various amount of water.

Table 4. Quantitative analytical results obtained by RIR method (wt%) of the fly ash after carbonation with various amounts of water.

Samples	Periclase	Lime	Calcite	Anhydrite	Quartz	Mullite	Hematite	Gehlenite	Halite	Sylvite
25-W/A	0.35	0.00	14.13	1.68	18.07	0.28	2.14	22.50	40.79	0.06
50-W/A	0.88	0.14	21.31	1.92	18.91	0.65	3.66	23.03	26.03	3.21
75-W/A	0.58	0.06	26.16	2.12	17.34	0.72	3.31	23.25	25.15	1.30
100-W/A	0.95	0.24	21.98	2.25	9.32	2.47	0.82	24.01	37.96	0.00

To investigate the properties of the fly ash with a small amount of water in the environments with low CO₂ concentrations, CO₂ captures were conducted at CO₂ concentrations of 10 (10-C/A), 20 (20-C/A), 50 (50-C/A), and 100% (100-C/A). The moisture content and reaction time were fixed at 20% and 10 min, respectively.

Figure 9 and Table 5 show the crystal structure of the fly ash after CO₂ capture using different concentrations of CO₂ and the amount of materials by using the relative intensity ratio (RIR) technique from the XRD. The CaCO₃ components of the 10-C/A, 20-C/A, 50-C/A, and 100-C/A were 15.21,

19.46, 19.86, and 21.98%, respectively. As shown in Table 5, the CaCO_3 component stabilized at CO_2 concentration of 20%. This result indicates that the semi-dry process can be applied to the power plant without a CO_2 concentration process.

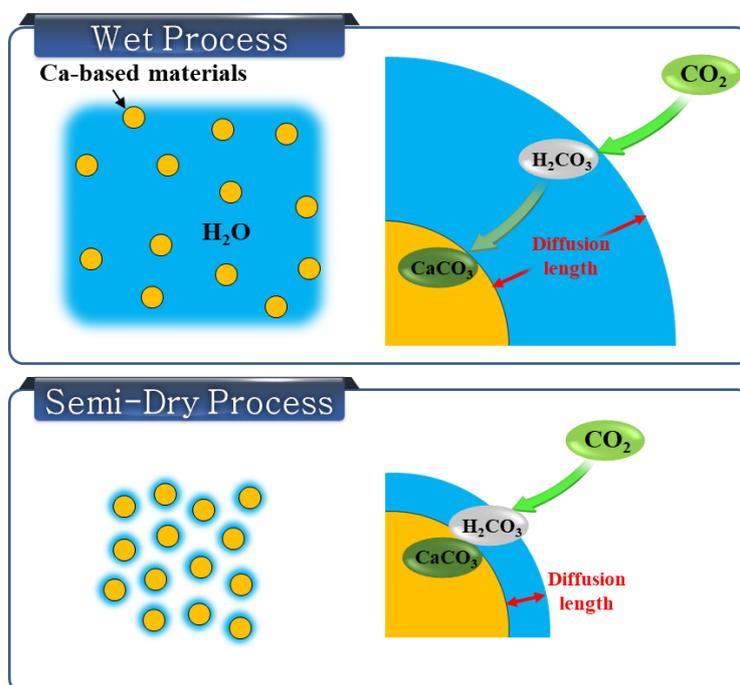


Figure 8. Schematic diagram of the semi-dry process and wet process for the CO_2 capture.

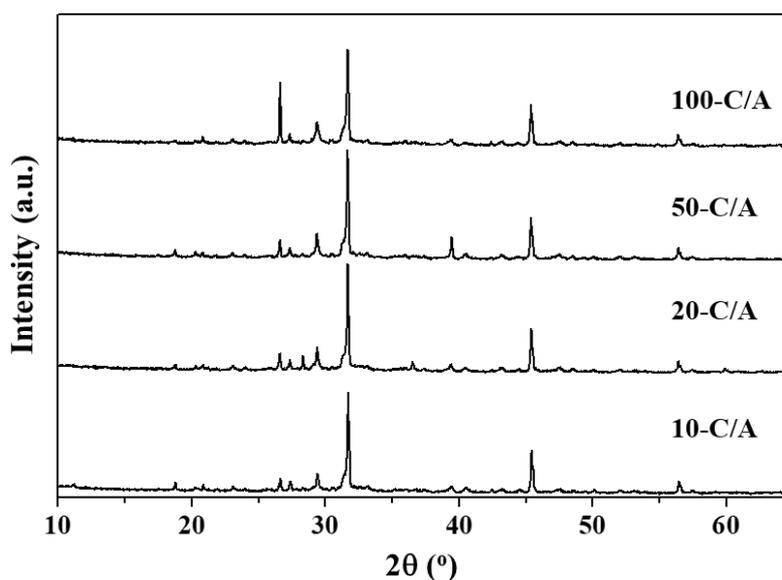


Figure 9. X-ray diffraction patterns of fly ashes after carbonation with various CO_2 concentrations.

Table 5. Quantitative analytical results obtained by RIR method (wt%) of the fly ash after carbonation with various CO_2 concentrations.

Samples	Periclase	Lime	Calcite	Anhydrite	Quartz	Mullite	Hematite	Gehlenite	Halite	Sylvite
10-C/A	0.34	0.00	15.21	1.56	14.32	1.09	1.22	25.11	40.79	0.06
20-C/A	0.34	0.02	19.46	1.33	11.35	0.84	1.39	24.39	38.34	2.54
50-C/A	0.38	0.01	19.86	1.12	14.84	0.33	0.91	22.55	38.72	1.17
100-C/A	0.95	0.24	21.98	2.25	13.17	2.47	0.82	24.01	37.96	0.00

Figure 10 and Table 6 show the crystal structure of the fly ash after CO₂ capture in a reaction time of 1 (1-T/A), 5 (5-T/A), 10 (10-T/A), and 30 min (30-T/A), and the amount of materials. The CaCO₃ component of the 1-T/A, 5-T/A, 10-T/A, and 30-T/A was 16.26, 15.16, 15.21, and 16.72%, respectively. As shown in Table 6, the carbonation performed well despite the short reaction time of 1 minute. This result indicates that the semi-dry process can be designed as a continuous process to capture large scales of CO₂.

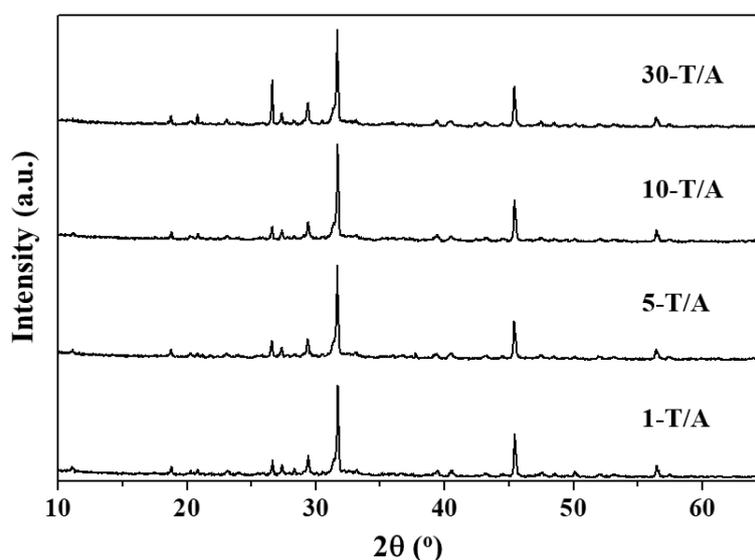


Figure 10. X-ray diffraction patterns of fly ashes after carbonation with various reaction times.

Table 6. Quantitative analytical results obtained by RIR method (wt%) of the fly ash after carbonation with various reaction times.

Samples	Periclase	Lime	Calcite	Anhydrite	Quartz	Mullite	Hematite	Gehlenite	Halite	Sylvite
10-C/A	0.34	0.00	15.21	1.56	14.32	1.09	1.22	25.11	40.79	0.06
20-C/A	0.34	0.02	19.46	1.33	11.35	0.84	1.39	24.39	38.34	2.54
50-C/A	0.38	0.01	19.86	1.12	14.84	0.33	0.91	22.55	38.72	1.17
100-C/A	0.95	0.24	21.98	2.25	13.17	2.47	0.82	24.01	37.96	0.00

4. Discussions

The utilization of SRF ash has emerged as one of the most important interventions in SRF power plants. Due to the calcium-based materials in the SRF ash, the SRF ash can be reused as a material for CO₂ capture. According to Loo et al., who studied the utilization of circulating fluidized bed combustion (CFBC) ash, high humidity conditions during the carbonation process were a critical factor that significantly enhanced the CO₂ uptake in the CFBC ash [17]. However, in this study, the results show that the high amount of water led to a low efficiency of carbonation reaction. This may be due to the fact that the diffusion length of the H₂CO₃ increased correlatively with the amount of water. These results demonstrate that the semi-dry carbonation process is more effective in the aspect of cost and time compared to the wet process. The carbonated SRF ash can be used in various construction industries such as a mineral admixture for concrete [23]. For the utilization of the carbonated SRF ash prepared via semi-dry carbonation process, further research should be conducted on controlling the conditions of the process such as temperature and pH value.

5. Conclusions

In this study, the utilization of the fly ash from SRF power plant as a solid sorbent material for CO₂ capture via semi-dry carbonation reaction was evaluated as a simple CO₂ reduction technique which does not require a high cost wastewater treatment plant and an evaporating process. Quantitative

analysis was conducted by using the relative intensity ratio technique from the XRD to study the potential for fly ash carbonation under semi-dry carbonation process. The amount of CO₂ capture increased as the amount of water increased. However, when the ratio of the ash-to-water was 1:1, the amount of CO₂ capture decreased because the diffusion length of the H₂CO₃, from the outside of the water to the calcium-based materials, increased with the increasing amount of water. The results indicated that H₂O plays an important role in the carbonation of calcium-based materials. The fly ash of 100 g can capture 10.17 g of CO₂ by semi-dry carbonation reaction without any treatment. The moisture content can affect the CO₂ capture capacity but CO₂ concentration and reaction time do not significantly affect the carbonation reaction. In the semi-dry carbonation process, the carbonation was well performed in the short reaction time and with low CO₂ concentration. These results show that the semi-dry process can be designed as a continuous process and applied to a power plant directly without CO₂ concentration processes.

Author Contributions: Conceived and wrote the manuscripts, J.H.K.; advice and revised the manuscript, W.T.K.; both authors agreed with the final version of manuscript.

Funding: National Research Foundation of Korea: 2017M3D8A2086035.

Acknowledgments: This research was supported by the National Strategic Project-Carbon Upcycling of the National Research Foundation of Korea (NRF) funded by the Ministry of Science and ICT (MSIT), the Ministry of Environment (ME) and the Ministry of Trade, Industry and Energy (MOTIE) (2017M3D8A2086035).

Conflicts of Interest: The authors declare no conflict of interest.

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