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Evaluation of Specimen Size Effect on Reaction Rates of CO_2 Fixation Tests of Fly Ash

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ABSTRACT: In the aim of achieving carbon neutrality by 2050, it is necessary to find suitable Carbon Capture Storage (CCS) materials, which have abundant sources and the ability to fix CO_2 with low cost and low energy consumption. Fly ashes are widely considered as promising CCS materials and their CO_2 fixation reaction has been researched massively. However, among these studies, there is a lack of study concerning the effect of fly ash specimen size on CO_2 fixation reaction. In this study, for evaluating specimen size effect on CO_2 fixation reaction, constant flow aeration type CO_2 fixation tests were conducted with different air flow rates on specimens with different heights and diameters. The CO_2 fixation reaction rates (k_1 and k_2) were calculated using two models: Langmuir monolayer adsorption model for k_1 in early reaction, and the unreacted nucleus model for k_2 in latter stage of the reaction, and the relation between the reaction rates and each parameter was investigated. It was found that specimen height showed negative correlations with k_1, while specimen height had minor effects on CO_2 fixation amount per unit mass ($m_{CO2\text{-}sample}$) and k_2. Additionally for specimens of different diameters, similar $m_{CO2\text{-}sample}$ values were observed at similar pore flow velocities. Pore flow velocities were found to have positive correlations with k_1 independent to specimen diameter, whereas no significant correlations were observed for k_2. From the above results, it was suggested that the effect of specimen size on $m_{CO2\text{-}sample}$ and CO_2 fixation reaction rates could be evaluated using pore flow velocity as a parameter.

KEYWORDS: Fly ash, CO_2 fixation, specimen size, kinetic model.

1 INTRODUCTION

In the aim of achieving carbon neutrality by 2050, it is necessary to find suitable Carbon Capture Storage (CCS) materials, which have abundant sources and the ability to fix CO_2 with low cost and low energy consumption. Fly ashes are considered as promising CO_2 fixation materials which can react with CO_2 in normal temperature and pressure conditions, thereby generating thermodynamically stable calcium carbonate crystals on its particle surface (Liu *et al*. 2012).

As a decarbonization strategy in the waste management sector, a carbon capture society system has been proposed in which CO_2 is fixed by fly ash using a CO_2 fixation plant, followed by either landfilling at final disposal sites or utilization as construction material. Schematic illustration of a carbon capture society system using a CO_2 fixation plant are shown in Figure 1.

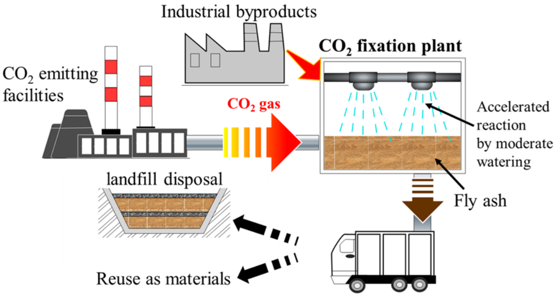


Figure 1. Schematic illustration of a carbon capture society system using a CO_2 fixation plant

To ensure efficient operation of the CO_2 fixation plant, it is important to optimize both the reaction time and CO_2 fixation amount. In particular, specimen size and air flow rate are critical design parameters, and their influence should be evaluated based on experimental results. However, while various studies (Komine *et al*. 2023; Wang *et al*. 2024; Yokoi *et al*. 2023) have investigated the carbonation behavior of fly ash, few have focused on the effect of specimen size CO_2 fixation efficiency.

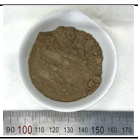
In this study, for evaluating specimen size effect on CO_2 fixation reaction, constant flow aeration type CO_2 fixation tests were conducted with different air flow rates on specimens with different heights and diameters. The CO_2 fixation reaction rates (k_1 and k_2) were calculated using two models (Suzuki *et al*. 2025), respectively, as: 1) Langmuir monolayer adsorption model for k_1 in early reaction, and 2) the unreacted nucleus model for k_2 in latter stage of the reaction. Finally, the relation between the reaction rates and each parameter was investigated.

2 MATERIAL AND TEST PROCEDURE

2.1 *Material*

In this study, Biomass Boiler Fly ash (BBF) was used. The fly ash BBF was generated from a biomass boiler, in which the fuel consisted of 70% wood pellets and 30% palm kernel shells (PKS). Previous studies (Suzuki *et al*. 2025; Yokoi *et al*. 2023) have confirmed that CO_2 can be fixed in BBF results in the formation of calcium carbonate ($CaCO_3$). The fundamental properties of BBF are shown in Table 1.

Table 1. The fundamental properties of BBF

Photo	
Particle density (Mg/m^3)	2.33
Natural water content (%)	0.16
Median particle diameter (mm)	0.024
pH	12.4
Calcium mass content (mass%)	15.7
Calcium dissolution concentration (mg/L)	1220

In table 1, the calcium mass contents were measured by X-ray fluorescence (XRF) spectrometer (ZSX Primus II, Rigaku). Calcium dissolution concentrations were measured using ion chromatography (Ion Analyzer IA-300, Toa-DKK Co., Ltd.) according to the Japanese Notification No. 46 of the Environment Agency in August 1991. To identify the calcium compounds responsible for the CO_2 fixation reaction, X-ray diffraction (XRD) analysis was conducted using a multipurpose diffractometer (RINT-Ultima III, Rigaku), and calcium oxide (CaO, lime) was identified as the dominant reactive phase in BBF.

2.2 *Test Procedure*

In this study, constant flow aeration type CO_2 fixation tests (Komine *et al*. 2023) were conducted, as illustrated in Figure 2.

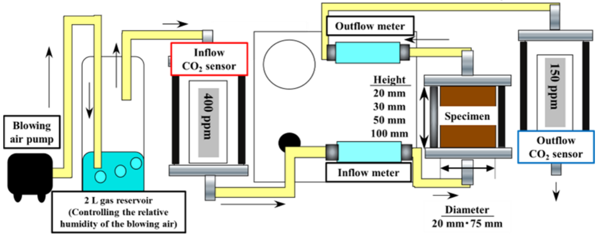


Figure 2. Schematic illustration of the constant flow aeration type CO_2 fixation test

In this test, a cylindrical column was filled with a sample adjusted to a target initial water content. According to previous research (Yokoi *et al.* 2023), for the fly ash sample BBF exhibits high reactivity and elevated average CO_2 fixation rates at an initial water content in the range of 20–40%. However, when the water content was adjusted to 30%, particle agglomeration occurred, significantly reducing air permeability and hindering reaction progress. Therefore, an initial water content of 20% was adopted for all experiments. The sample was loosely packed without compaction. Laboratory air, with a CO_2 concentration ranging from 400 to 1000 μL/L, was blown through the specimen at a constant flow rate. Previous studies (Liu *et al.* 2012; Wang *et al.* 2024) have shown that higher relative humidity in the supplied air enhances the CO_2 fixation reaction. Therefore, in this test, laboratory air was humidified to a relative humidity of 90±5% by passing it through a 2L gas reservoir filled with distilled water before being introduced into the specimen.

The amount of CO_2 fixed was quantified by the concentration difference between the upstream CO_2 concentration before entering the column C_{in} (μL/L) and the downstream CO_2 concentration after passing through the specimen C_{out} (μL/L). The test was terminated at the time defined as t_{end} (hour), when the ratio C_{out}/C_{in} exceeded 1.0 for the first time after the start of the test. The cumulative amount of CO_2 fixed by the specimen $m_{CO_2}^{SUM}$ was calculated using Equation (1).

$$m_{\mathrm{CO_2}}^{\mathrm{SUM}} = \int_0^{t_{\mathrm{end}}} \left(Q_{\mathrm{in}} \cdot \frac{C_{\mathrm{in}} - C_{\mathrm{out}}}{10^6} \cdot \frac{T_0}{T} \cdot \frac{p}{p_0} \cdot \frac{M_{\mathrm{CO_2}}}{V_{\mathrm{m}}} \right) dt \qquad (1)$$

where, $m_{CO_2}^{SUM}$ (g-CO_2) represents the cumulative amount of CO_2 fixed in the specimen, Q_{in} (L/min) is the air flow rate, C_{in} and C_{out} (μL/L) are the upstream and downstream CO_2 concentrations, respectively. T_0 (273K) and p_0 (1.013×10^5 Pa) represent the standard temperature and pressure, while T (K) and p (Pa) represent the actual temperature and pressure during testing. M_{CO_2} is the molecular weight of CO_2 (44 g/mol), and V_m is the molar volume of gas (22.4 L/mol). The amount of CO_2 fixed per unit dry mass of the sample $m_{CO_2\text{–sample}}$ was calculated using Equation (2).

$$m_{\mathrm{CO_2-sample}} = \frac{m_{\mathrm{CO_2}}^{\mathrm{SUM}}}{m_s} \qquad (2)$$

where, $m_{CO_2\text{–sample}}$ (g-CO_2/g-sample) is the amount of CO_2 fixed per unit dry mass of the specimen, and m_s (g-sample) is the dry mass of the material used to prepare the specimen. Since data were recorded every 60 seconds, the time variation of the CO_2 fixation amount per unit dry mass was calculated based on equation (2). In this study, the CO_2 fixation performance of each sample was evaluated based on the amount of CO_2 fixed per unit dry mass. Additionally, the CO_2 fixation reaction ratio α was calculated using Equation (3).

$$\alpha = \frac{m_{\mathrm{CO_2}}^{\mathrm{t}}}{m_{\mathrm{CO_2}}^{\mathrm{SUM}}} \qquad (3)$$

where, $m_{CO_2}^{t}$ (g-CO_2) represents the cumulative amount of CO_2 fixed in the specimen between $t = 0$ and time t. The reaction ratio α was defined as 1.0 at t_{end}, and its the temporal variation was used to construct the reaction rate curve.

In this study, for evaluating specimen size effect on CO_2 fixation reaction, constant flow aeration type CO_2 fixation tests were conducted with different air flow rates on specimens with different heights and diameters. Four specimen heights, 20, 30, 50, and 100 mm, were tested while maintaining a constant specimen diameter of 75 mm. Additionally, two specimen diameters, 20 mm and 75 mm, were examined with a fixed specimen height of 20 mm. Since comparing specimens of different diameters under a constant air flow rate does not allow for appropriate evaluation of the size effects, the pore flow velocity was used as a unified parameter. Pore flow velocity v (m/min) was calculated using Equation (4).

$$v = \frac{Q_{\mathrm{in}} \times 10}{\frac{n}{100} \cdot \left(\frac{D}{2}\right)^2 \cdot \pi} \qquad (4)$$

where, n (%) is the porosity, and D (mm) is the specimen diameter. All specimens were prepared with a constant initial water content of 20% and dry density, and laboratory air was supplied at a flow rate adjusted to achieve equivalent pore flow velocity.

3 DETERMINATION METHOD OF REACTION RATE CONSTANTS BASED ON KINETIC MODELS

In this study, the carbonation reaction of fly ash in contact with CO_2 was modeled as a two-step process following, previous studies (Fernandez *et al.* 2004; Liu *et al.* 2012) as: 1) the early stage and 2) later stage. In the early stage of the reaction is controlled by interfacial chemical kinetics, while the later stage is controlled by diffusion through the product layer. To represent these two distinct rate-controlling mechanisms, a hybrid kinetic model was applied: the Langmuir monolayer adsorption model for the early stage, and the unreacted nucleus model for the later stage (Suzuki *et al.* 2025). This approach allows the independent estimation of two reaction rate constants including: 1) reaction rate constant in early stage (k_1) and 2) reaction rate constant in later stage (k_2). These two rate constants were determined using Equation (5) and (6), respectively.

$$\alpha = 1 - e^{-k_1 t} \qquad (5)$$

$$1 - \frac{2}{3}\alpha - (1-\alpha)^{\frac{2}{3}} = k_2 t \qquad (6)$$

Methodology for determining reaction rate constants is shown in Figure 3. To appropriately apply kinetic models to each stage, it is essential to identify the transition point (t') on the reaction ratio curve, where the governing mechanism shifts from surface-reaction control to diffusion control. This point corresponds to the time when the reactive surface sites are fully covered with calcium carbonate. However, since the fly ash used in this study is a heterogeneous material with varying calcium content among particles, it is unlikely that carbonation progresses uniformly across all particles. Therefore, it is assumed that the reaction becomes diffusion-controlled beyond t'. During the diffusion-controlled stage, the reaction ratio α is theoretically proportional to the square root of time, allowing the curve to be approximated by a linear function. Accordingly, t' was defined as the earliest time at which the coefficient of determination (R^2) for the linear approximation from t' to t_{end} exceeds 0.98.

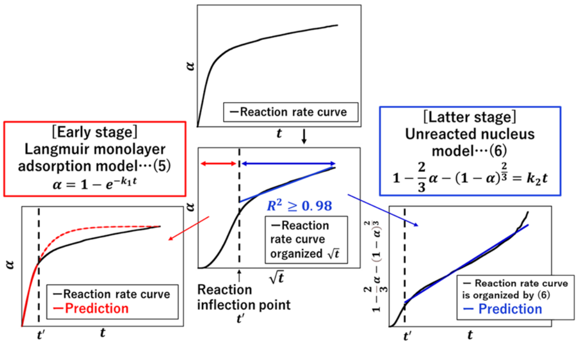


Figure 3. Methodology for determining reaction rate constants (Suzuki *et al*. 2025)

Based on this criterion, the rate constant k_1 (min^{-1}) was estimated by minimizing the difference between the experimental reaction ratio curve and Equation (5) over the interval from the start of the test to t'. The rate constant k_2 (min^{-1}) was determined from the slope of the linear approximation using Equation (6) in the interval from t' to t_{end}.

4 EVALUATION OF SPECIMEN SIZE EFFECT

4.1 *Effect of specimen height*

The results of the CO_2 fixation tests conducted with varying specimen heights are summarized in Table 2. The relationship between specimen height and $m_{CO2\text{-}sample}$ are shown in Figure 4. It was found that $m_{CO2\text{-}sample}$ remained nearly constant across all specimen heights, indicating that specimen height had little effect on $m_{CO2\text{-}sample}$.

Table 2. The results of the CO_2 fixation tests conducted with varying specimen heights

Case	1	2	3	4
Sample Height (mm)	20	30	50	100
Sample diameter (mm)	75			
Air flow rate (L/min)	1.41			
Dry density ($\mathrm{Mg/m^3}$)	0.478	0.502	0.463	0.498
Initial water content (%)	18.6	18.8	19.6	20.2
Water content after experiment (%)	3.87	2.78	4.72	4.50
CO_2 fixation duration (hour)	117.5	166.8	164.9	212.9
CO_2 fixation amount per unit mass (g-CO_2/g-sample)	0.0222	0.0231	0.0242	0.0222

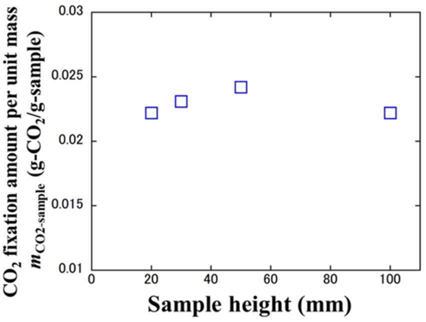


Figure 4. The relationship between specimen height and $m_{CO2\text{-}sample}$

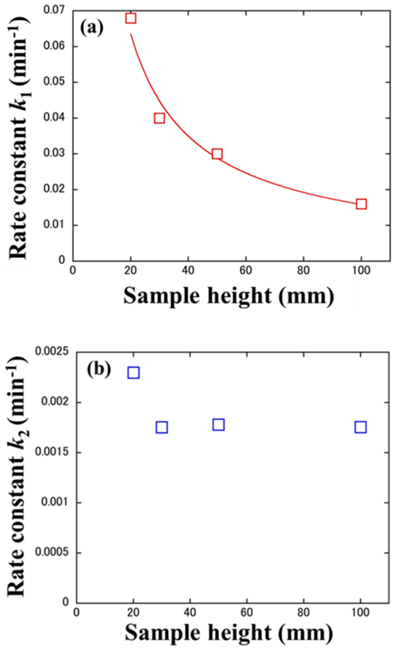


Figure 5. The relationship between specimen height and (a) k_1; (b) k_2

The relationship between specimen height and the reaction rate constants k_1 and k_2 are shown in Figure 5. It was found that specimen height showed negative correlations with k_1, which is attributed to surface-reaction-controlled kinetics in the early stage of carbonation. As specimen height increases under constant dry density, m_s also increases, leading to a reduction in available reactive surface area per unit mass and thus a lower apparent reaction rate. Additionally, greater specimen height may increase resistance to airflow, reducing CO_2 availability in deeper layers, and further diminishing k_1.

The slightly elevated value of k_2 observed at a specimen height of 20 mm may be attributed to fluctuations in the upstream and downstream CO_2 concentrations (C_{in} and C_{out}), which were influenced by human activity and the operation of nearby laboratory equipment. In contrast, k_2, representing the

Table 3. The results of CO_2 fixation tests conducted under different specimen diameters

Case	1	2	3	4	5	6	7	8	9	10	11
Sample Height (mm)	20										
Sample diameter (mm)	20							75			
Air flow rate (L/min)	0.10	0.20	0.25	0.30	0.40	0.50	0.60	1.41	2.81	4.22	5.63
Dry density ($\mathrm{Mg/m^3}$)	0.473	0.472	0.477	0.479	0.478	0.451	0.483	0.475	0.473	0.473	0.457
Pore flow velocity (m/min)	0.399	0.798	1.001	1.202	1.601	2.002	2.409	0.401	0.798	1.198	1.586
Initial water content (%)	19.8	19.7	19.7	19.7	19.3	19.0	20.0	19.3	20.0	19.2	19.4
Water content after experiment (%)	7.26	3.66	5.61	6.83	4.73	8.44	4.24	6.88	5.85	3.40	3.51
CO_2 fixation duration (hour)	102.6	74.5	41.3	20.8	16.9	17.2	16.5	79.2	83.3	16.4	18.9
CO_2 fixation amount per unit mass (g-CO_2/g-sample)	0.0233	0.0228	0.0178	0.0146	0.0148	0.0155	0.0145	0.0223	0.0225	0.0162	0.0152

diffusion-controlled stage of the reaction, remained generally constant regardless of specimen height. It was suggested that the diffusion process is governed by the microscopic structure of the calcium carbonate product layer and is largely independent of bulk specimen geometry.

4.2 *Effect of specimen diameter and flow rate*

The results of CO_2 fixation tests conducted under different specimen diameters are shown in Table 3.

The relationship between pore flow velocity and $m_{\mathrm{CO2\text{-}sample}}$ are shown in Figure 6. When $v \leq 1.0$ m/min, $m_{\mathrm{CO2\text{-}sample}}$ were consistent with values reported in previous studies. However, when pore flow velocity exceeded 1.0 m/min, $m_{\mathrm{CO2\text{-}sample}}$ decreased and approached a constant lower value. It was suggested that the presence of a pore flow velocity near 1.0 m/min, beyond which the CO_2 fixation efficiency declines. Additionally, Table 3 shows that the CO_2 fixation duration was significantly reduced under high pore flow velocity conditions (i.e., $v \geq 1.0$ m/min). To investigate the influence of pore flow velocity on the CO_2 fixation reaction, the reaction rate constants k_1 and k_2 were calculated.

The relationship between pore flow velocity and the reaction rate constants k_1 and k_2 are shown in Figure 7. For different specimen diameters, similar k_1 and k_2 values were observed at similar pore flow velocities. It was suggested that the effect of specimen diameter and flow rate on $m_{\mathrm{CO2\text{-}sample}}$ and CO_2 fixation reaction rates could be evaluated using pore flow velocity as a parameter.

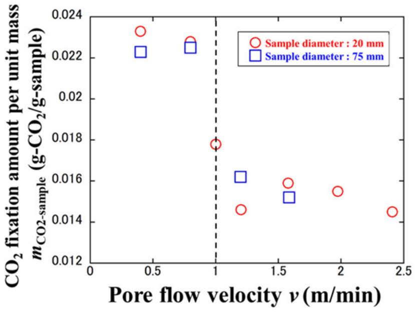


Figure 6. The relationship between pore flow velocity and $m_{\mathrm{CO2\text{-}sample}}$

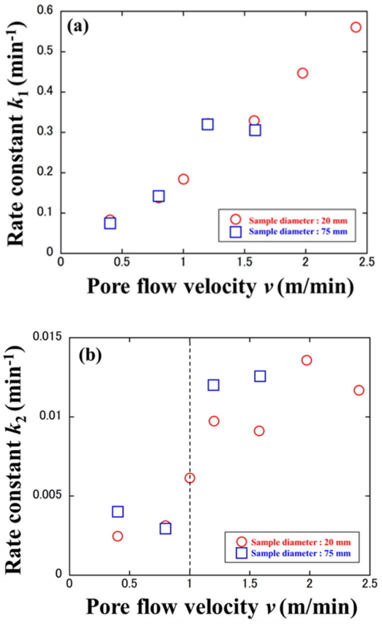


Figure 7. The relationship between pore flow velocity and (a) k_1; (b) k_2

Furthermore, pore flow velocities were found to have positive correlations with k_1 independent of specimen diameter, whereas no significant correlations were observed for k_2. As pore flow velocities exceeding 1.0 m/min, k_2 exhibited consistently high. Since k_2 represents the diffusion rate through the calcium carbonate layer formed on the particle surface, it is inferred that lower $m_{\mathrm{CO2\text{-}sample}}$ corresponds to higher values of k_2. These findings suggest that while the reaction rate in the early stage is primarily governed by the CO_2 supply rate (i.e., pore flow velocity), the influence of pore flow velocity diminishes in the later stage.

5 CONCLUSIONS

1) It was found that specimen height showed negative correlations with k_1. While specimen height had minor effects on CO_2 fixation amount per unit mass ($m_{\mathrm{CO2\text{-}sample}}$) and k_2.
2) For specimens of different diameters, similar $m_{\mathrm{CO2\text{-}sample}}$ values and k_1 and k_2 were observed at similar pore flow velocities.
3) Pore flow velocities were found to have positive correlations with k_1 independent to specimen diameter, whereas no significant correlations were observed for k_2.
4) It was suggested that the effect of specimen diameter and flow rate on $m_{\mathrm{CO2\text{-}sample}}$ and CO_2 fixation reaction rates could be evaluated using pore flow velocity as a parameter.

6 ACKNOWLEDGEMENTS

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7 REFERENCES

Fernandez Bertos, M., Simons, S. J., Hills, C. D., Carey, P. 2004. A review of accelerated carbonation technology in the treatment of cement-based materials and sequestration of CO_2. *Journal of Hazardous Materials*, 112(3), 193–205. https://doi.org/10.1016/j.jhazmat.2004.04.019

Komine, H., Yokoi, K., Taga, H., Saito, Y., Suzuki, K. 2023. Fundamental study on the creation of a carbon capture urban environment using CO_2 fixation materials. *Japanese Journal of JSCE*, 79(4), 22-00051.

Liu, W., An, H., Qin, C., Yin, J., Wang, G., Feng, B., Xu, M. 2012. Performance enhancement of calcium oxide sorbents for cyclic CO_2 capture—A review. *Energy & Fuels*, 26(5), 2751–2767. https://doi.org/10.1021/ef300220x

Suzuki, H., Komine, H., Wang, H., Ito, D., Suzuki, K., Kunihiro, A. 2025. Inference of kinetic model based on reaction mechanism in CO_2 fixation using soot and dust containing calcium cation. *Japanese Geotechnical Journal*, 20(1), 91–101.

Wang, C., Jiang, H., Miao, E., Wang, Y., Zhang, T., Xiao, Y., Liu, Z., Ma, J., Xiong, Z., Zhao, Y., Zhang, J. 2024. Accelerated CO_2 mineralization technology using fly ash as raw material: Recent research advances. *Chemical Engineering Journal*, 488, 150676. https://doi.org/10.1016/j.cej.2024.150676

Yokoi, K., Komine, H., Goto, S., Wang, H., Ito, D., Suzuki, K., Kunihiro, A., Hikida, T. 2023. Experimental study on CO_2 fixation by three types of fly ash – Effect of average particle size and Ca^{2+} leaching on the CO_2 fixation reaction rate. *Japanese Geotechnical Journal*, 18(2), 97–107.