Iron and Steel Slag Properties and Mechanisms for Carbon Dioxide Fixation in a Low-carbon Society

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ABSTRACT: This report presents carbon dioxide (CO_2) fixation properties of an iron and steel slag containing calcium, in order to contribute to a geotechnical application for the formation of a sound material-cycle society and a low-carbon society. To investigate the properties of CO_2 fixation, CO_2 fixation tests with constant flow were conducted. Results show that when the CO_2 concentration 4500 $\mu L_{-CO_2}/L$ was flowed in a specimen by 0.05 L/min, for a non-aged steelmaking slag, the amount of CO_2 fixed was the maximum: 0.04 g_{-CO_2}/g_{-slag}. The amount of CO_2 fixed in the steelmaking slag resulted from about 20% of soluble calcium in the chemical reaction. Therefore, it is possible that the quantity of CO_2 fixation can be evaluated from the viewpoint of the mechanism of CO_2 fixation using the quantity of water-soluble calcium.

KEYWORDS: Iron and steel slag, Carbon dioxide, Calcite, Low-carbon society, Sound material-cycle society

1. INTRODUCTION

In recent years, actions for reduction of greenhouse gases are conducted to produce a low-carbon society. Especially, carbon dioxide (CO_2) accounts for over 90% of greenhouse gases. CO_2 concentrations on earth have been increasing because of deforestation and the use of fossil fuels since the Industrial Revolution. Global warming is an important issue for geotechnical engineering as well because sea-level rises and heavy rains raise the likelihood of liquefaction. Given that background, technical development is strongly required to decrease atmospheric CO_2 concentrations and CO_2 emissions. CO_2 capture and storage is studied at present as a technology to reduce atmospheric CO_2.

The Fundamental Law for Establishing a Sound Material-Cycle Society was promulgated in 2000. Utilization of waste materials for the construction of a recycling society is demanded in Japan. Such cyclical use of resources is important to minimize the need for newly obtained natural resources and to limit discharge of waste into natural environments.

In light of the current conditions described above, some CO_2 fixation technology must be developed using waste materials to support waste utilization and the reduction of atmospheric CO_2 concentrations. Previous studies related to CO_2 fixation of waste materials show that CO_2 can be fixed by waste concrete, iron, and steel slag. Several modes of fixing CO_2 use pressure, water, temperature and humidity as necessary conditions for chemical reactions. However, the CO_2 fixation properties of waste in atmospheric conditions (atmospheric pressure, normal temperature and pressure) have not been investigated sufficiently. Previous studies show that iron and steel slag have high fixation potential of CO_2. Table 1 shows categories of iron and steel slag, which are by-products discharged from processing of iron and steel products. They are classified mainly as blast furnace slag (BFS) and steelmaking slag (SS).

Actually, BFS, which is discharged from blast furnaces that produce pig iron during melting separation, consists of non-ferrous iron ore and limestone as auxiliary materials and ash from coke. Furthermore BFS is classified as air-cooled blast furnace slag (A-BFS) or granulated blast furnace slag (G-BFS) based on the slag cooling. However, SS is discharged in the steelmaking process for manufacturing the steel. Converter slag, used for various iron and steel slag applications, is cooled slowly by natural cooling and water spraying in a cooling yard. Electric arc furnace slag is generated when iron scrap is melted and refined. Each year in Japan, BFS and SS are discharged respectively in 24,838 kt and 15,079 kt amounts. Therefore, slag use is extremely necessary. Some new technology must be developed for the beneficial use of the slag.

The initial objective in this study is investigation of SS and BFS characteristics in atmospheric conditions when used as a geo-material for low-cost CO_2 fixation with low environmental impact.

Table 1 Category of an iron and steel slag

Iron and steel slag	Blast furnace slag (BFS)	Air-cooled blast furnace slag (A-BFS)
		Granulated blast furnace slag (G-BFS)
	Steel making slag (SS)	Converter slag (CS)
		Electric arc furnace slag (EFS)

2. CO_2 FIXATION TEST OF IRON AND STEEL SLAG

This section presents experimental procedures used for CO_2 fixation test with constant CO_2 gas flow and procedures used for estimation of the CO_2 fixed in the sample. Figure 1 is a schematic image of the CO_2 fixation test apparatus. Figure 2 shows that the test simulates a cover soil of final disposal site in which CO_2 flux is given by filled waste. As shown in Figure 3, the column system was used to assess CO_2 fixation properties of the iron and steel slag with a constant gas flow rate.

2.1 Test samples

Fundamental properties of the slags used in the CO_2 fixation test are presented in Table 2. Four kinds of iron and steel slags were prepared: air-cooled blast furnace slag (A-BFS), granulated blast furnace slag (G-BFS), non-aged steelmaking slag (non-aged SS), and aged steelmaking slag (aged SS).

The SS is usually distributed for use after aging to prevent slag particle expansion (aged SS). Non-aged SS is not distributed to markets. The non-aged SS is expected to fix more CO_2 than the aged SS because aged SS fixes CO_2 during aging. Therefore, both were used to compare the amounts of fixed CO_2. The slag particle density of the samples, natural water contents, and the amounts of calcium (Ca) elution are presented in Table 2. A soil particle density test (JIS

A 1202) was conducted to measure the slag particle density. The amount of Ca elution was estimated using batch elution tests based on the test specified in the Public Notice No, 46 of the Ministry of Environment (JLT-46), Japan. These samples have 33–44% of CaO. Grain sizes of samples used for this study were adjusted from 0.425 mm to 2.0 mm.

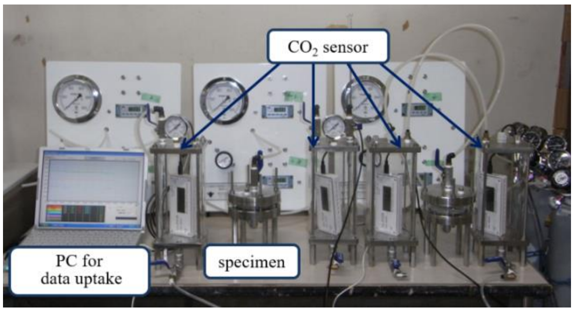


Figure 1 Apparatus for CO_2 fixation test

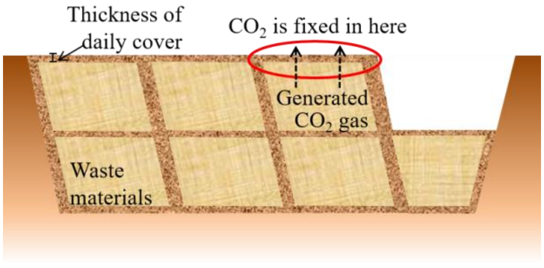


Figure 2 Daily cover of final landfill site

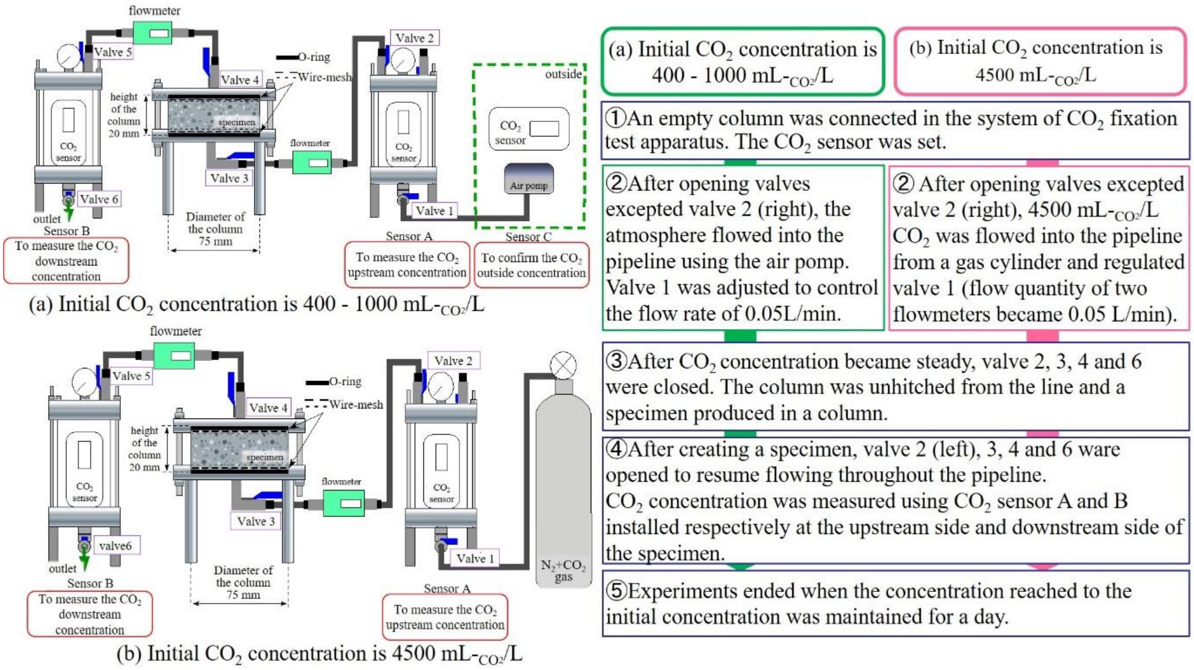
Table 2 Fundamental properties of slags

(a) Slag particle density, natural water content and Ca elution amount

	Density of slag particle [g/cm^3]	Water content [%]	Ca elution [mg/L]
A-BFS	2.96	6.66	440
G-BFS	2.81	4.72	5.0
Aged SS	3.39	6.70	740
Non-aged SS	3.37	8.47	790

(b) Chemical components

Component	A-BFS and G-BFS [%]	Aged SS and Non-aged SS [%]
SiO_2	34.8	15.7
CaO	43.8	41.1
Al_2O_3	14.1	2.0
MgO	5.0	7.5
P_2O_5	0.9	2.5
S	0.0	0.0
TiO_2	0.5	0.8
MnO	0.2	4.7
Cr_2O_3	0.0	0.1
Na_2O	0.2	0.0
K_2O	0.3	0.0
Total-Fe	0.3	5.5



(a) Initial CO_2 concentration is 400 - 1000 mL-$_{CO_2}$/L

(b) Initial CO_2 concentration is 4500 mL-$_{CO_2}$/L

(a) Initial CO_2 concentration is 400 - 1000 mL-$_{CO_2}$/L

(b) Initial CO_2 concentration is 4500 mL-$_{CO_2}$/L

①An empty column was connected in the system of CO_2 fixation test apparatus. The CO_2 sensor was set.

②After opening valves excepted valve 2 (right), the atmosphere flowed into the pipeline using the air pomp. Valve 1 was adjusted to control the flow rate of 0.05L/min.

② After opening valves excepted valve 2 (right), 4500 mL-$_{CO_2}$/L CO_2 was flowed into the pipeline from a gas cylinder and regulated valve 1 (flow quantity of two flowmeters became 0.05 L/min).

③After CO_2 concentration became steady, valve 2, 3, 4 and 6 were closed. The column was unhitched from the line and a specimen produced in a column.

④After creating a specimen, valve 2 (left), 3, 4 and 6 ware opened to resume flowing throughout the pipeline. CO_2 concentration was measured using CO_2 sensor A and B installed respectively at the upstream side and downstream side of the specimen.

⑤Experiments ended when the concentration reached to the initial concentration was maintained for a day.

Figure 3 Apparatus and experimental procedure of the column type CO_2 fixation test

2.2 Experimental method of CO_2 fixation test

The experimental conditions are shown in Table 3. Concentrations of two kinds of CO_2 were used: 400–1000 µL-$_{CO2}$/L and 4500 µL-$_{CO2}$/L in the CO_2 fixation test. The concentration of 4500 µL-$_{CO2}$/L was controlled by mixing nitrogen (N_2) gas. First, an empty column was connected in the system of CO_2 fixation test apparatus as shown in Figure 3. After opening valves, except for the right side of valve 2, the gas flowed into a pipe line using the air pump. Valve 1 was adjusted to control the gas flow rate at 0.05 L/min. The range of measurements of the gas flowmeter was 0.05–5.00 L/min. The accuracy was ±3% of the reading value. Gas circulation was continued for about 3 h until steady CO_2 concentration in the whole pipe line. After CO_2 the concentration became steady, valves 2, 3, 4, and 6 were closed. The column was unhitched from the line. Then a specimen was produced in a column. In this regard, air continued to flow during making the specimen. Air was exhausted from the left side of valve 2.

Table 3 Test conditions and the amount of fixed CO_2 (specimen height is 60 mm)

	Gas volume of inflow [L/min]	Initial CO_2 concentration [mg/L]	Temperature [K]	Test time [min]	Dry density [g/cm^3]	Initial water content [%]	Water content of after test [%]	Amount of fixed CO_2 [g-$_{CO2}$]	Amount of fixed CO_2 per unit of mass [g-$_{CO2}$/g-$_{slag}$]
A-BFS	0.05	532	296±2	1800	1.38	6.66	0.75	3.2	0.009
G-BFS		513		490	0.91	4.72	0.89	0.0	0.000
Aged-SS		500		2590	1.61	7.96	1.03	4.0	0.010
Non-aged SS		499		2750	1.55	8.04	1.33	4.2	0.014
A-BFS	0.05	4561	296±2	190	1.08	6.66	0.65	4.2	0.014
Aged-SS		4560		400	1.57	7.98	0.98	9.8	0.023
Non-aged SS		4572		400	1.55	8.04	1.12	14.2	0.034

A specimen was produced by division into three layers. Each sample fell from 50 mm in the column. The 75-mm-diameter column was 20 mm high or 60 mm high. After creating a specimen, valve 2 of the right side was closed. Then valve 2 of the left side, and valves 3, 4, and 6 were opened to resume flowing throughout the pipeline. At this moment, the averaged holding time of the CO_2 in the specimen was about 2 min for the case of 60 mm height and about 1 min for the case of 20 mm height. The CO_2 concentration was measured using CO_2 sensors A and B installed respectively at the upstream side and downstream side of the specimen. The possible range of measurement using CO_2 sensors is 0–5000 L-$_{CO2}$/L. The rated precision is 5% of ± 30 L-$_{CO2}$/ L reading value.

The initial value of CO_2 was recorded at the start. Experiments ended when the concentration reached the initial concentration and the concentration was maintained for a day.

For a mixed gas of N_2 and CO_2, the CO_2 concentration was 4500 L-$_{CO2}$/L, a high-pressure gas container was connected to the apparatus. Figure 3(b) shows that experimental procedures were identical to the CO_2 fixation tests using atmosphere.

2.3 Calculation of the amount of fixed CO_2

The amount of fixed CO_2 of the slag was calculated using the CO_2 concentration measured in this test (Figure 4). The CO_2 concentration ratio (C/C_0) was defined as the ratio of the CO_2 concentration in a specimen downstream side (C [L-$_{CO2}$/L]) to the initial CO_2 concentration in the downstream side (C_0 [L-$_{CO2}$/L]). The amount of fixed CO_2 M [g-$_{CO2}$] is shown in Eq. (1).

$$M = \sum_{t=0}^{t_{end}} \left(V_{in} \times \frac{C_0 - C}{10^6} \times \frac{T_0}{T} \times \frac{p}{p_0} \times \frac{M_{CO_2}}{V} \right) \quad (1)$$

In that equation, V_{in} [L/min] stands for the gas volume of inflow in 1 min, T [K] represents the gas temperature. The temperature and pressure of an ideal gas are, respectively, T_0 [K] and p_0 [kPa]. t_{end} [min] denotes the elapsed time when C/C_0 reached 1.0.

2.4 CO_2 fixation amount of iron and steel slag

Table 3 presents test conditions and amounts of fixed CO_2 for a specimen with 60 mm height and initial CO_2 concentration equal to that of the atmosphere. The relation between C/C_0 and elapsed time is shown in Figures 5(a) and 5(b).

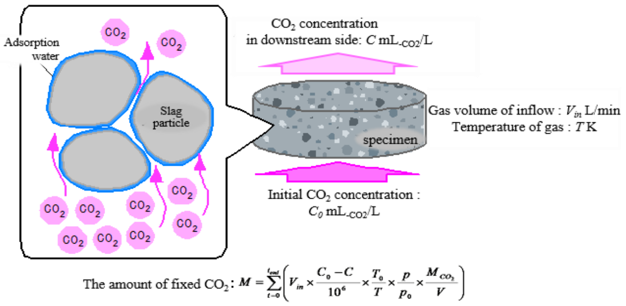


Figure 4 Conceptual diagram of the fixed CO_2 amount calculation

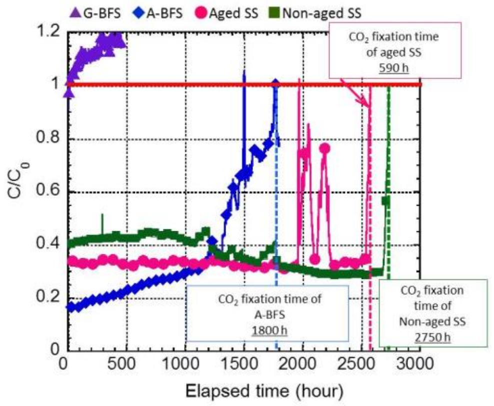
First, in Figure 5, C/C_0 of the granulated blast furnace slag (G-BFS) increased 0.2 after 500 h from starting. Actually, G-BFS only slightly fixed CO_2 because the CO_2 concentration of downstream side did not decrease from initial CO_2 concentration. Table 2 shows that the G-BFS had a low amount of Ca elution. Therefore, it is presumed that CO_2 cannot react with Ca^{2+} around slag particles.

However, C/C_0 of air-cooled blast furnace slag (A-BFS), aged steelmaking slag (aged SS), and non-aged steelmaking slag (non-aged SS) decreased respectively approximately 0.15, 0.35, and 0.45 within 1 h from the test start. After that, C/C_0 increased gradually to 1.0 in terms of the A-BFS, aged SS and non-aged SS. Unstable behavior of CO_2 concentration was observed for the aged SS after 2000 h from starting. After C/C_0 of the A-BFS reached 1.0, reduction of the C/C_0 was also observed from the influence of CO_2 concentration outside. Therefore after confirming that C/C_0 became stable and the value was maintained at 1.0 during 1 day, testing was stopped. The time from test starting to the test end was defined as the CO_2 fixation time. That time was 1800 h (about 2.5 months) for A-BFS, 2590 h (about 3.6 months) for aged SS, and 2750 h (about 3.8 months) for non-aged SS. Regarding the amount of fixed CO_2 calculated using Eq. (1), A-BFS was 3.2 g, aged SS was 4.0 g, and non-aged SS was 4.2 g. The amount of fixed CO_2 per unit mass is calculable by dividing M by the mass of the slag. The value of A-BFS was 0.009 g-$_{CO2}$/g-$_{slag}$. That of aged SS was 0.010 g-$_{CO2}$/g-$_{slag}$. That of non-aged SS was 0.014 g-$_{CO2}$/g-$_{slag}$.

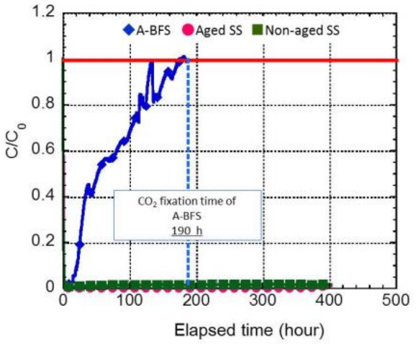
According to the experimentally obtained results, A-BFS, aged SS and non-aged SS can fix CO_2. The experiment was conducted with 4500 $\mu L_{-CO_2}/L$ initial CO_2 concentration and 60 mm specimen height. The relation between *C/C₀* and elapsed time is shown in Figure 5(b). Regarding A-BFS, the CO_2 concentration ratio reached 1.0 at approximately 190 h from starting. The amount of fixed CO_2 was 4.2 g. The amount of CO_2 fixation per unit of slag mass was 0.014 g_{-CO_2}/g_{-slag}.

Then, this study evaluated CO_2 fixation of A-BFS, aged SS, and non-aged SS in the experiments with 4500 $\mu L_{-CO_2}/L$ initial CO_2 concentration and 60 mm specimen height. The relation between C/C_0 and elapsed time is shown in Figure 5(b). Regarding A-BFS, the CO_2 concentration ratio reached 1.0 from the experiment start in approximately 190 h. The amount of fixed CO_2 was calculated using Eq. (1) as 4.2 g. The amount of fixed CO_2 per unit of slag mass was 0.014 g_{-CO_2}/g_{-slag}. Therefore, based on the initial CO_2 concentration and 4500 $\mu L_{-CO_2}/L$, about 1.5 times more CO_2 was fixed than with atmospheric concentration. However, the aged and non-aged SS did not increase to the C/C_0 during approximately 400 h of the examination time although they fixed the CO_2 of 9.8 g and 14.2 g for each sample. These samples had such high CO_2 fixation capacity that the capacity to fix CO_2 exceeded the capacity of the CO_2 gas cylinder. Therefore, this study used a 20-mm-high specimen to produce a sample with less mass.

Table 4 shows test conditions and the fixed CO_2 amounts in the case of 20 mm height of both aged and non-aged SS. Figure 6 shows the relation between C/C_0 and elapsed time. The C/C_0 of aged SS was reached 1.0 by approximately 180 h. The C/C_0 of non-aged SS also reached 1.0 in the same duration. When exchanging amounts of CO_2 which each SS fixed to that per unit of slag mass, the amount of fixed CO_2 normalized by the mass of the sample was 0.030 g_{-CO_2}/g_{-slag} for the aged SS and 0.040 g_{-CO_2}/g_{-slag} for the non-aged SS. Results show that the potential CO_2 fixation of non-aged SS was higher than that of aged SS.



(a) Initial CO_2 concentration is 400–1000 $\mu L_{-CO_2}/L$



(b) Initial CO_2 concentration is 4500 $\mu L_{-CO_2}/L$

Figure 5 Relation between C/C_0 and elapsed time (60 mm)

Table 4 Test conditions and the amount of CO_2 fixation (specimen height is 20 mm)

	Gas volume of inflow [L/min]	Initial CO_2 concentration [mg/L]	Temperature [K]	Test time [min]	Dry density [g/cm^3]	Initial water content [%]	Water content of after test [%]	Amount of fixed CO_2 [g_{-CO_2}]	Amount of fixed CO_2 per unit of mass [g_{-CO_2}/g_{-slag}]
Aged-SS	0.05	4859	296±2	180	0.97	8.47	0.98	3.0	0.030
Non-aged SS		4572		180	0.95	10.8	1.12	3.6	0.041

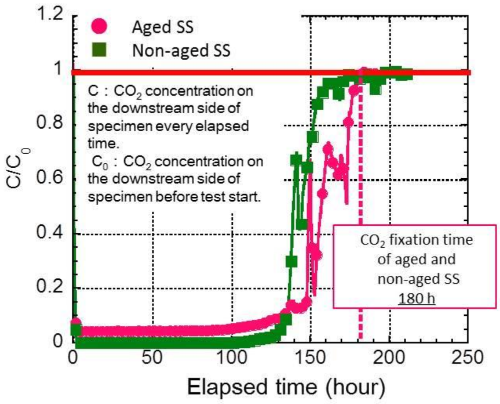


Figure 6 Relation between C/C_0 and elapsed time (initial CO_2 concentration is 4500 $\mu L_{-CO_2}/L$, specimen height is 20 mm)

2.5 Influence of specimen water contents on CO_2 fixation

The previous section showed that a case of 4500 $\mu L_{-CO_2}/L$ fixed about 1.5 times more CO_2 than the same conditions with atmospheric concentration. The amount of fixed CO_2 depended on Ca elution quantity because the CO_2 fixation progress is predicted by a reaction of Ca^{2+} in a sample and atmospheric CO_2. However, the amount of fixed CO_2 differed for identical samples: the quantity of Ca elution was the same in the samples. Tables 3 and 4 show that the difference CO_2 fixation resulted from sample drying because water contents of the test specimens decrease after the examination.

The CO_2 fixation test was additionally conducted using non-aged SS with examination periods of 24, 72, 96, 120, and 192 h. The amounts of fixed CO_2 and water contents of the specimens were measured after the examination. Figure 7 shows the relation between the amounts of fixed CO_2 and the water contents of the specimens along with elapsed time. The water contents of the specimen decreased along with the examination period. The water contents of the specimens became approximately 1.5% after 200 h of gas flow. The amount of fixed CO_2 decreased rapidly for more than 120 h; then the specimen water contents reached 2.0%. In addition, after adding distilled water to the specimen, the CO_2 concentration ratio decreased again, as shown in Figure 8, which suggests recovery of capacity of CO_2 fixation of sample dried. Results show that a reason for decreasing CO_2 fixation is the decrease in water contents of the sample during the examination.

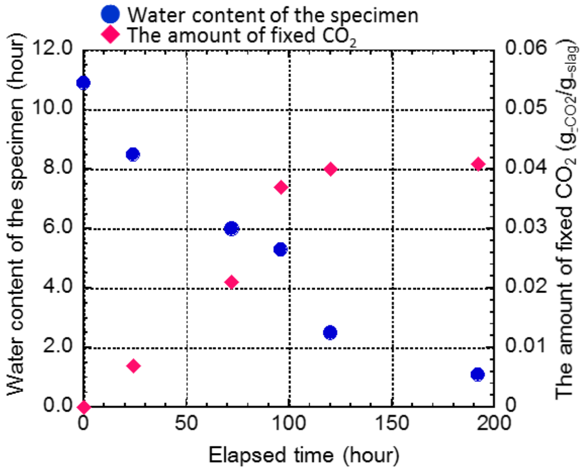


Figure 7 Relation between the amount of fixed CO_2 and the water content of the specimen

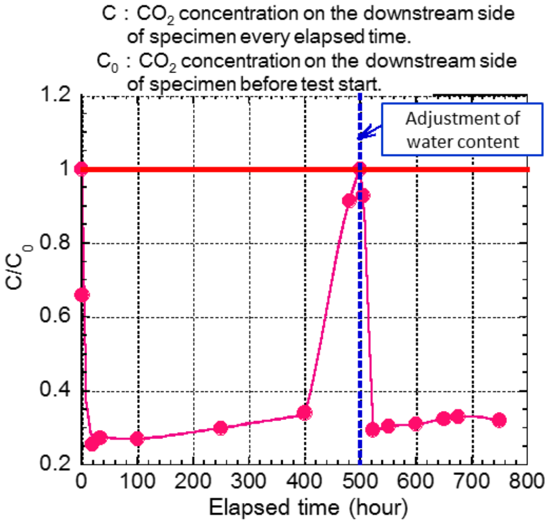


Figure 8 Effect of adding distilled water of specimen

3. MECHANISMS OF SLAG CO_2 FIXATION

As described in section 2, the amount of fixed CO_2 of the steelmaking slag (SS) was estimated using the quantity of decrease in the CO_2 concentration during circulation of the CO_2 gas in the experiment. In this section, secondary minerals of the slag reacted with CO_2 gas were analyzed using powder X-ray diffractometry (XRD). Furthermore, carbonate content tests were conducted. Mechanisms of the CO_2 fixation of the slag are discussed.

3.1 Samples

The non-aged SS after the CO_2 fixation test, as shown in Table 2, was used for XRD and carbonate content tests. As described above, SS was prepared by aging to prevent particle expansion. Therefore, CO_2 had already been fixed at the initial state. Non-aged SS was used to investigate carbonation during experiments in this study to elucidate the mechanism of CO_2 fixation.

3.2 Change of mineral composition by CO_2 fixation

To elucidate the mechanism of the CO_2 fixation, the mineral composition of the non-aged SS was investigated using XRD with the non-aged SS before and after the CO_2 fixation testing.

Figure 9 presents the XRD results, particularly addressing the minerals including calcium (Ca), which included approximately 30% as CaO in non-aged SS. Comparing the XRD pattern of the SS before and after the CO_2 fixation tests, a peak of calcium hydroxide ($Ca(OH)_2$) was observed in both samples.

Especially, the peak strength of $Ca(OH)_2$ was higher in the sample before the CO_2 fixation test. However, for the sample after the CO_2 fixation test, the peak strength of $Ca(OH)_2$ was lower. It is noteworthy that a peak of calcium carbonate ($CaCO_3$) was observed in the sample after the CO_2 fixation test. The amount of Ca elution as shown in Table 2(b) originated from $Ca(OH)_2$, which is an important chemical for CO_2 fixation of the materials. Presumably, CO_2 was fixed as $CaCO_3$ through a chemical reaction of Eq. (2).

$$\begin{aligned} CO_2 + H_2O &\rightarrow HCO_3^- + H^+ \\ Ca(OH)_2 &\rightarrow Ca^{2+} + 2OH^- \\ Ca^{2+} + HCO^{3-} &\rightarrow CaCO_3 + H^+ \end{aligned} \tag{2}$$

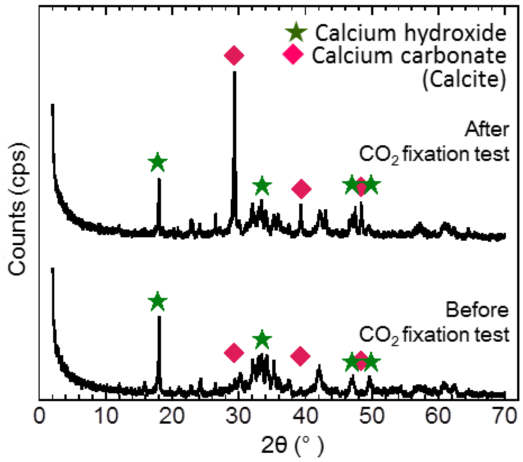


Figure 9 Mineral composition was changed of non-aged SS

3.3 Change of carbonate content by the CO_2 fixation

Based on XRD results, which indicated $CaCO_3$ generation after the CO_2 fixation test, carbonate contents of the slags before and after the CO_2 fixation test were investigated. Measurements of carbonate contents of the slags were conducted, referring to the procedure proposed in a previous report. Actually, $CaCO_3$ reacts with hydrochloric acid (HCl) in a closed rigid cell with a pressure gauge. CO_2 gas pressure is measured according to Eq. (3).

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2\uparrow \tag{3}$$

3.3.1 Experimental procedure of carbonate content test

Figure 10 presents the apparatus and the experimental procedures used for the carbonate content tests. First, calibration tests were conducted to ascertain the relation between the generated CO_2 gas pressure and the amount of carbonate used in a reaction in Eq. (3). Commercial calcium carbonate ($CaCO_3$) was used for this study. The amounts of $CaCO_3$ put in a small case were 0.02, 0.06, 0.10, and 0.12 g. Figure 10 shows that $CaCO_3$ and 20 mL of 3 mol hydrochloric acid (HCl) were put in the 45-mm-high acrylic reaction column of 75 mm diameter. After sealing up the column, $CaCO_3$ in a small case was reacted with HCl by laying the vessel for the sample. The CO_2 gas pressure increased gradually through the chemical reaction shown as Eq. (3). In the equilibrium state, the relation prevails between the pressure and the mass of $CaCO_3$ used in the reaction. Next, the carbonate content of the unknown sample was measured. The sample mass was 0.50 g because the carbonate contents of the unknown sample were less than those of pure $CaCO_3$.

3.3.2 Calculation of the generated carbonate amount

In the controlled sample, the relation between the pressure and the mass of $CaCO_3$ is shown in Figure 11. The calibration curve used to estimate carbonate contents are presented in Eq. (4).

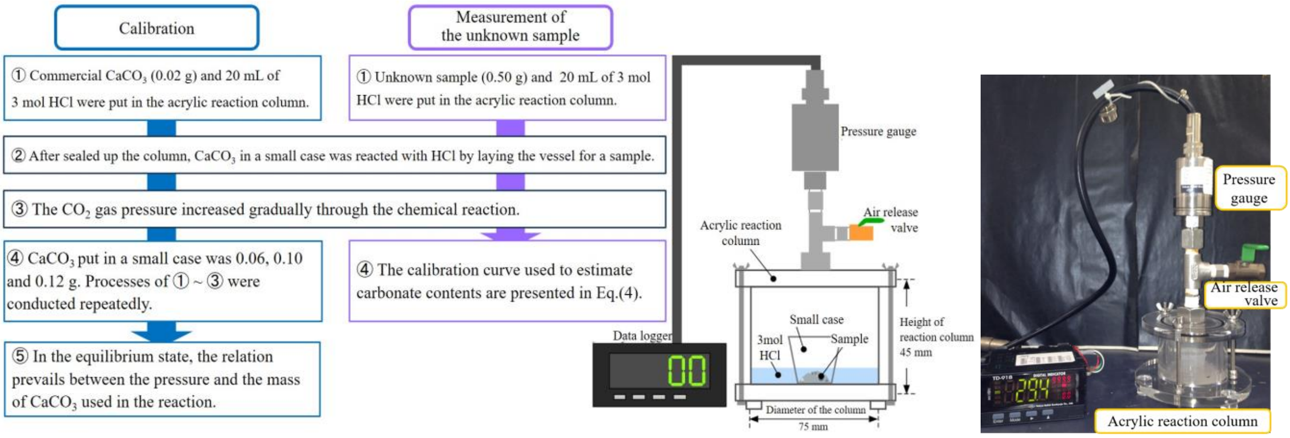


Figure 10 Apparatus and experimental procedure of the carbonate content test

$$Y = X / 613.9 \tag{4}$$

Therein, Y represents the mass of $CaCO_3$ corresponding to carbonation content; X is the gas pressure. In addition, the carbonate contents of the specimen before and after the CO_2 fixation test were estimated using the gas pressure measured by the examination. The specimen after the CO_2 fixation test was divided into four pieces by cutting every 5 mm from the upper part. In addition, the carbonate formed during the CO_2 fixation test was calculated using Eq. (5) based on results of carbonate content tests.

$$M' = Y_a - Y_b \tag{5}$$

Therein, M' [g] stands for the quantity of generated carbonate by the CO_2 fixation test, Y_b [g] and Y_a [g] respectively denote the carbonate contents before and after CO_2 fixation in the samples. Net generated carbonate is defined as the difference between the carbonate content after the CO_2 fixation (Y_a) and the carbonate content before CO_2 fixation (Y_b) because non-aged SS would slightly fix CO_2 during storage in a laboratory. M was normalized by the slag mass, m' [g-$_{CaCO3}$/g-$_{slag}$].

Figure 12 shows the distribution of the generated carbonate content in the specimen. The generated carbonate content decreased drastically at the upper 5 mm part of the specimen. Presumably, the decrease in the amount of fixed CO_2 occurred by drying of the sample before contacting CO_2 at the upper part of the specimen. Precipitation of $CaCO_3$ requires water. Therefore, CO_2 fixation progresses in the adsorption water of the SS particle surface (Figure 13). Water contents in the specimen decreased by as much as 2% during 200 h from the start, as described in section 2.5. The SS was unable to fix CO_2 by the decrease in adsorption water in the CO_2 fixation test using the 20-mm-high specimen. Therefore, it was difficult to fix CO_2 in upper part of the specimen.

The amount of fixed CO_2 calculated from the CO_2 fixation test was 3.6 g. That estimated from the generated carbonate content was 3.9 g. Comparing the amount of fixed CO_2 in section 2 to the estimate from carbonate content showed that each value was almost identical. Therefore, it can be found that most fixed CO_2 in the specimen is precipitated as $CaCO_3$ in the CO_2 fixation test.

4. EVALUATION OF THE AMOUNT OF FIXED CO_2 OF SS

This section describes estimation of fixed CO_2 using Ca elution based on the CO_2 fixation mechanism, in addition to evaluation of the reduction of CO_2 concentration in an environment of aged and non-aged SS.

4.1 CO_2 fixation ratio

The CO_2 fixation ratio m_{rate} [%] is defined as the ratio of fixed CO_2 m_{CO2} [mol] and the maximum amount of fixed CO_2 $m_{\max}$ [mol] as revealed from the availability test for CO_2 fixation of the sample.

$$m_{rate} = \frac{m_{CO_2}}{m_{\max}} \times 100 \tag{6}$$

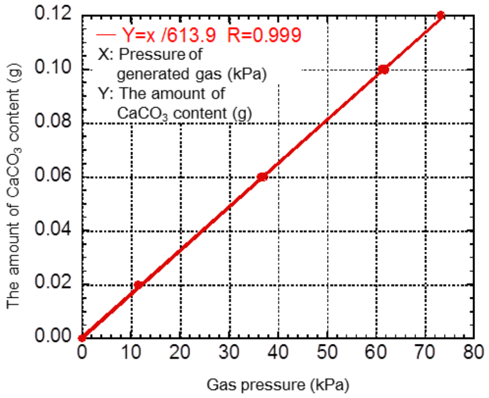


Figure 11 Relation between the pressure and the mass of $CaCO_3$

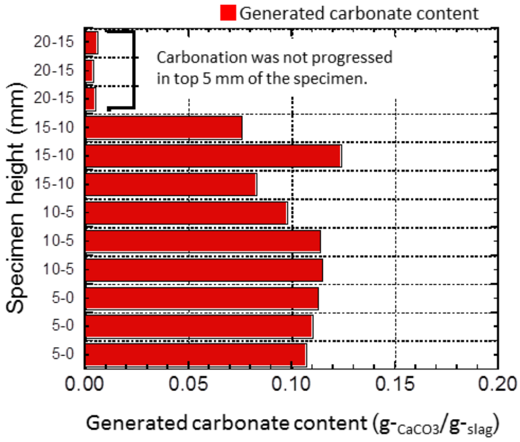


Figure 12 Distribution of generated carbonate content in the specimen

Figure 14 shows a concept diagram of the CO_2 fixation ratio by Eq. 6. Actually, CO_2 fixation is caused by Ca ions reaching from non-aged SS. The possible Ca elution was determined by the availability test (NEN7371). A possible maximum amount of fixed CO_2 in this study was calculated using the possible Ca elution because of the relation between soluble Ca of the slag and CO_2 fixation (Figure 13). The CO_2 fixation ratio was calculated by comparing the possible maximum amount of fixed CO_2 $m_{\max}$ in the steel slag to the amount of fixed CO_2 m_{CO2} estimated using the CO_2 fixation test.

4.2 Availability test

To quantify the leachable cations from aged and non-aged SS, the availability test, standardized as NEN7371, was conducted. The apparatus for the availability test is shown in Figure 15. The test uses pH conditions of two kinds: (1) neutral condition and (2) acid condition. First, 500 mL of distilled water and 50 g of the sample as dry mass that had been crushed under 125 µm of grain size were put in a 1 liter container. The liquid–solid ratio was 10. The mixture was stirred at 200±20 rpm for 3 h.

The mixture was stirred, maintaining pH 6.7–7.5. For pH adjustment, 1 mol/L nitric acid (Wako Pure Chemical Industries, Ltd.) was used. After 20 min from end of stirring, the mixture was centrifuged in 3000 rpm for 20 min. Supernatant solution was filtered using a membrane filter of 0.45 µm pore size for liquid–solid separation. The collected liquid was designated as “solution 1.” Second, the collected solid sample after centrifuging was put in 500 mL of distilled water. The residual sample on the filter paper and the equipment was also collected by washing with distilled water, which included 500 mL for second testing. In the second, pH was maintained as 3.9–4.1. Stirring the mixture and liquid–solid separation were conducted as they were in step 1. The supernatant solution after filtration was designated as “solution 2.” Cation concentrations (Na^+, K^+, Mg^{2+}, Ca^{2+}) of test solutions 1 and 2 were measured using inductively coupled plasma (ICP-AES). The total elution of cations from the solutions was defined as the total release of cation for the sample.

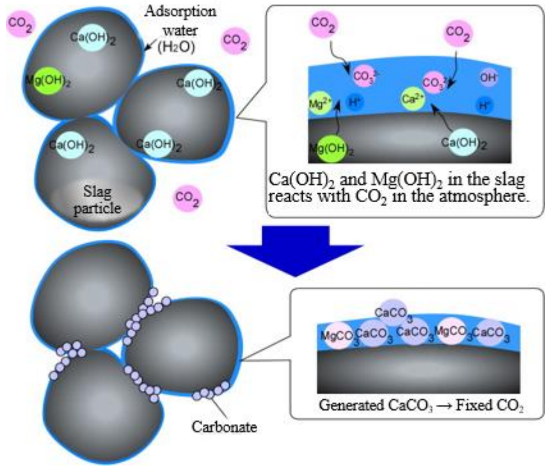
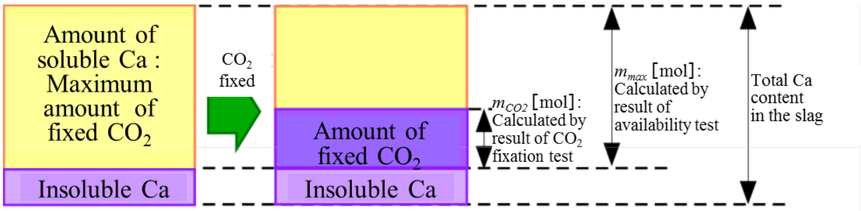
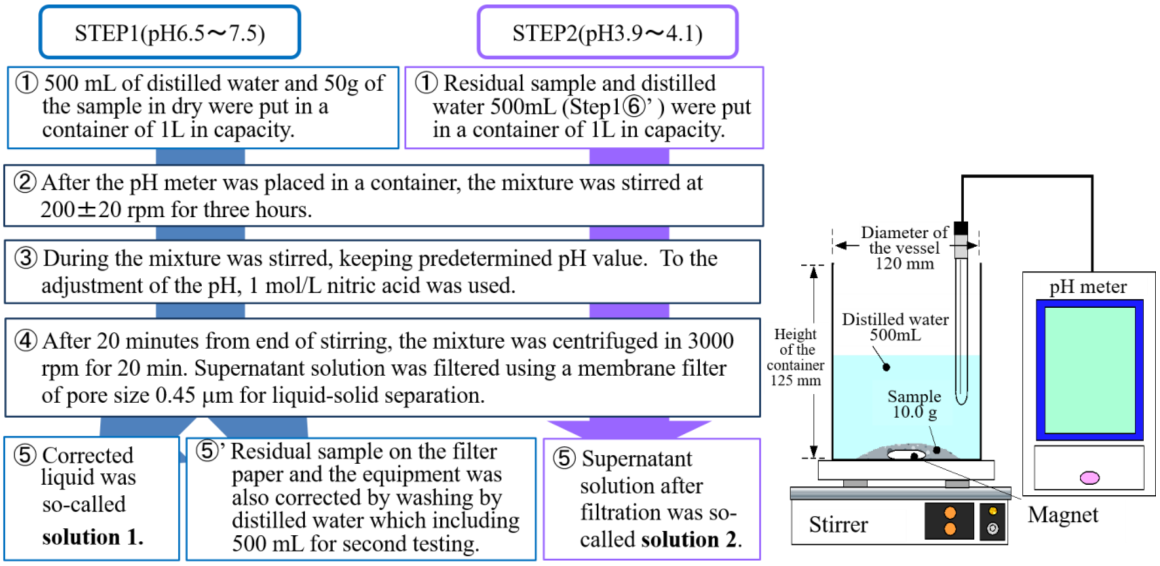


Figure 13 Conceptual diagram of CO_2 fixation mechanism



$$\text{CO}_2 \text{ fixation ratio [\%]} \quad : m_{rate} = \frac{m_{CO_2}}{m_{max}} \times 100$$

Figure 14 Conception diagram of the CO_2 fixation ratio


STEP1(pH6.5～7.5)

① 500 mL of distilled water and 50g of the sample in dry were put in a container of 1L in capacity.

STEP2(pH3.9～4.1)

① Residual sample and distilled water 500mL (Step1⑥’) were put in a container of 1L in capacity.

② After the pH meter was placed in a container, the mixture was stirred at 200±20 rpm for three hours.

③ During the mixture was stirred, keeping predetermined pH value. To the adjustment of the pH, 1 mol/L nitric acid was used.

④ After 20 minutes from end of stirring, the mixture was centrifuged in 3000 rpm for 20 min. Supernatant solution was filtered using a membrane filter of pore size 0.45 µm for liquid-solid separation.

⑤ Corrected liquid was so-called **solution 1.**

⑤’ Residual sample on the filter paper and the equipment was also corrected by washing by distilled water which including 500 mL for second testing.

⑤ Supernatant solution after filtration was so-called **solution 2**.

Figure 15 Apparatus and experimental procedure of the availability test

4.3 CO_2 fixation ratio and CO_2 calculated using eluted cation

The eluted cation from the particle of SS reacts to CO_2 dissolved in the adsorption water, as shown in the conceptual diagram of CO_2 fixation: Figure 13. Formation of carbonate is presented in Eq. 2. The aged and non-aged SS have larger amounts of leachable Ca^{2+}, as presented in Table 5. The generated carbonate was confirmed using XRD, as described in section 3. It was expected that the amount of maximum CO_2 fixation can be calculated using the Ca elution quantity. The amount of Ca^{2+} elution was approximately 1500 mg/L in aged SS and 1600 mg/L in non-aged SS. The amount of eluted Ca^{2+} from steelmaking slag converted into the amount of fixed CO_2 was 0.07 mol for the specimen. The CO_2 fixation ratio was about 23% according to calculations using Eq. 6 because the mole ratio of Ca and CO_2 in Eq. 2 is 1 to 1. Furthermore, the amount of fixed CO_2 of non-aged SS was 0.37 mol; its CO_2 fixation ratio was 20%. Therefore, about 20% and 30% of soluble Ca became immobilized by generation of $CaCO_3$ in the SS with the experimental conditions of the CO_2 fixation test, for which the initial CO_2 concentration was about 4500 $\mu L_{-CO2}/L$, and flow was 0.05 L/min.

Table 5 Result of availability test by aged and non-aged SS

	Ca^{2+} [mg/L]	Mg^{2+} [mg/L]	Na^{+} [mg/L]	K^{+} [mg/L]
Aging SS	1467	1	1	27
Non-aged SS	1623	14	3	4

Based on theoretical estimation, it can be expected that the CO_2 fixation ratio of the slag remained in 20% because of drying of the sample, as shown in section 2.5. The CO_2 fixation test would be continued with addition of moisture to investigate the maximum amount of fixed CO_2 of the samples.

When using SS as a CO_2 fixation material, it is plausible that the fixed CO_2 amount could be predicted theoretically if the amount of Ca elution of the sample were measured.

5. CONCLUSION

The study investigated CO_2 fixation characteristics of SS and BFS at atmospheric conditions for use as a geo-material because of proposed low-cost CO_2 fixation with low environmental impact. Results show that a-BFS, aged SS, and non-aged SS had CO_2 fixation effects. Especially, the amount of fixed CO_2 of the SS became greatest in the case of 4500 $\mu L_{-CO2}/L$ of initial CO_2 concentration. The amount of fixed CO_2 of aged SS was almost 0.03 g_{-CO2}/g_{-slag}. Therefore, it can be a CO_2 fixation material in addition to its current uses. The amount of fixed CO_2 of non-aged SS was almost 0.04 g_{-CO2}/g_{-slag}. Today, SS is usually distributed for use after aging to prevent slag particle expansion. Non-aged SS is not distributed to markets. According to the CO_2 fixation tests conducted for this study, the amount of fixed CO_2 of non-aged SS was 0.01 g_{-CO2}/g_{-slag} greater than that of aged SS. It seems justifiable to examine brand-new uses of non-aged SS in future studies.

X-ray diffractometry and carbonate content tests were conducted to clarify the CO_2 fixation mechanisms of the slag. Results show that most fixed CO_2 existed as $CaCO_3$ in the specimen. Based on the amount of Ca elution investigated using the availability test, the amount of fixed CO_2 was evaluated theoretically. The CO_2 fixation test in this study showed that aged and non-aged SS were able to fix CO_2 by almost 23% and 20% of the Ca amount.

Consequently, it is possible to contribute to reduction of greenhouse gases and the formation of a sound material-cycle society by encouragement of the beneficial use of SS, which has CO_2 fixation properties. The CO_2 concentration, water contents, and particle sizes of the sample, specimen density, and CO_2 gas pressure affect the CO_2 fixation of the slag. Therefore, it is important to investigate the related conditions in future studies.

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