

# Immobilization of Carbon Dioxide using Blast Furnace Slag fused with NaOH: A Comparative Study

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**Abstract**— In this study, we attempted a new immobilization method using blast furnace (BF) slag (by-product from steel-making plant) fused with NaOH. BF slag was treated with NaOH at 600 °C for 6 hours to obtain the fused slag, the fused slag was dissolved into distilled water to prepare the fused slag slurry, and CO<sub>2</sub> was injected into the fused slag slurry to immobilize CO<sub>2</sub> as calcium carbonate (CaCO<sub>3</sub>). This method is also compared with the conventional method for CO<sub>2</sub> immobilization using the slurry of BF slag powder and NaOH solution. CO<sub>2</sub> can be immobilized using the fused slag slurry as calcite. In this experimental condition, CO<sub>2</sub> was dissolved into the solution within 30 min, and then the CO<sub>2</sub> dissolved into the solution was reacted with calcium content dissolved from the fused slag to form calcite crystals. On the other hands, conventional method can mainly immobilize CO<sub>2</sub> by absorption of NaOH solution with the formation of a little amount of calcite. These results indicate that effective CO<sub>2</sub> immobilization is possible using BF slag fused with NaOH, in comparison with the slurry of BF slag powder and NaOH solution.

**Keywords**—Blast Furnace Slag, Carbon Dioxide Fixation, Alkali Fusion, Calcite

## I. INTRODUCTION

Global greenhouse gas (GHG) emissions have grown by more than 45 % since 1990, which has resulted in an increase in the atmospheric carbon dioxide (CO<sub>2</sub>), concentration from 350 ppm in 1990 to 391 in 2011 [1,2]. Thus, without the implementation of any CO<sub>2</sub> reduction measures, it is estimated that annual global CO<sub>2</sub> emissions will reach 58 Gt in 2050 [3]. However, to limit the increase of the global average temperature to 2 °C [4, 5], global CO<sub>2</sub> emissions have to be reduced by at least 50 % by 2050 compared to the 2010 level followed by a successive implementation of global carbon neutrality and net zero GHG emissions by the end of this century [1, 3]. Increasing greenhouse gas concentration, especially CO<sub>2</sub>, is the most significant factor influencing global temperature increases. To minimize the impact of CO<sub>2</sub> emissions, concentrations of CO<sub>2</sub>

should be stabilized by reducing its release into the atmosphere [6].

The amount of CO<sub>2</sub> emissions in Japan is the world's fourth largest (1.2 billion tons) in 1999, and annual CO<sub>2</sub> emission from the steel industry is the largest (170 million tons) among Japanese industries. Japan is the world's second largest steel producer, and its suppression, collection and immobilization of CO<sub>2</sub> is considered to be important.

There are several methods established for CO<sub>2</sub> sequestration such as geologic storage and ocean storage [7, 8], and mineral carbonation. Among these various approaches, mineral carbonation is considered to be an interesting method that involves the process by which CO<sub>2</sub> is removed from the atmosphere and is sequestered in stable minerals that are formed through its reaction [9-11]. The main advantage of mineral carbonation is that it implies an exothermic reaction, and yields to the formation of thermodynamically stable products. Additionally, this technology also exhibits a great CO<sub>2</sub> sequestration capacity due to the high availability of minerals deposits and it is cost-effective.

In steel-making, a large amount of solid alkaline by-products are formed. These slags contain elements, such as calcium, magnesium, iron and silicon in oxide forms. Blast furnace (BF) slag is the greatest byproduct of iron and steel-making processes, and more than 25 millions tons of BF slag is generated every year in Japan [12]. Although it has been widely used for cement production, road construction and as a concrete aggregate, the capacity for use of recycled BF slag in these fields has become saturated and the development of value-added products from such waste slag become an important issue for sustainability [13]. Therefore, research has recently been made in various recycling processes [14-17].

CO<sub>2</sub> immobilization technology in exhaust gas using BF slag has been investigated. The immobilization method using blast furnace slag is a method of immobilizing it as calcium carbonate by the reaction of calcium oxide in the slag and CO<sub>2</sub> on the surface of slag particles. Therefore, it is important to promote the reaction between CO<sub>2</sub> gas and calcium content in the slag. In our laboratory, the solubility of BF slag by alkali fusion treatment and fused slag was converted into functional materials, such as zeolites, tobermorite, hydrocalumite and so on [18-21].

However, alkaline fusion process was considered to be unsuitable for practical use because high temperature is required for fusion treatment. In the case of steel slag, slag is originally the molten state with about 1500 °C temperature, and is forcibly cooled to produce slag without utilizing large amounts of sensible and latent heats. Therefore, there is a possibility that fusion treatment can be performed efficiently by adding alkali salts during this cooling to produce alkali fused slag without adding extra high energy. Since the fused slag obtained by this method is alkaline material with high solubility, the dissolved solution is alkaline and the almost calcium component in the slag dissolves in the solution and precipitates as calcium hydroxide or calcium carbonate in the alkaline solution. Therefore, there is a possibility that CO<sub>2</sub> can be efficiently immobilized in the slurry because the fused slag can absorb carbon dioxide by the alkaline solution and immobilized by the formation of calcium component. However, there have been no reports to immobilize carbon dioxide by alkali-fused slag.

In this study, we attempted a new effective method for carbon dioxide immobilization using BF slag via alkali fusion, in comparison with conventional method using BF slag and NaOH solution. This suggests a new method to simultaneously solve the two problems for new use of industrial by-products, BF slag, using unutilized heat energy at steelworks and reduction of carbon dioxide emissions from steelworks.

## II. EXPERIMENTAL

### A. Sample Preparation

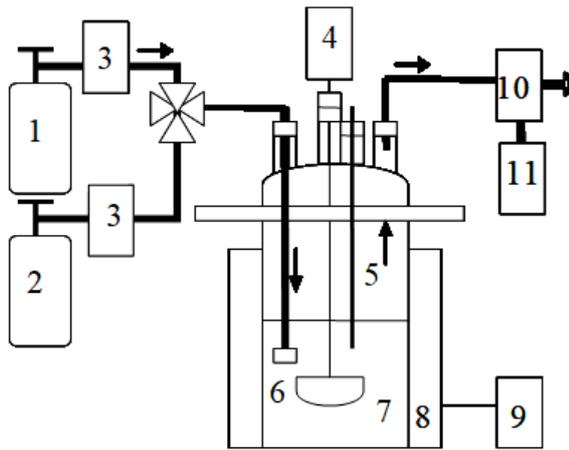
BF slag can be divided into air- and water-cooled slag according to the cooling method. These slags contain crystalline and amorphous phases, respectively. The BF slag used in this study (received from one of the steel-making plants in Japan) was water-cooled because water-cooled slag was used for CO<sub>2</sub> immobilization as conventional method of carbonation. The BF slag was ground by mill and sieved to under 1 mm. Ten grams of the slag was mixed with 16 g of NaOH powder and ground to obtain a homogeneous mixture. This mixture was then heated in a nickel crucible in an air atmosphere at 600 °C for 6 hours. The resultant material was cooled to room temperature, ground again and sieved to under 250 μm to obtain the fused slag. The chemical compositions of raw slag and fused slag were obtained by X-ray fluorescence spectrometry (XRF) (Shimadzu, XRF-1700) (Table 1). Raw slag was mainly composed of CaO (42.9 wt%), SiO<sub>2</sub> (34.5 wt%) and Al<sub>2</sub>O<sub>3</sub> (13.7 wt%), and some minor elements. After alkali fusion, the obtained precursor contained higher amounts of Na<sub>2</sub>O (57.3 wt%) and lower amounts of CaO (21.8 wt%), SiO<sub>2</sub> (11.8 wt%) and Al<sub>2</sub>O<sub>3</sub> (5.1 wt%) than the raw slag, caused by the NaOH addition.

TABLE I. CHEMICAL COMPOSITION OF RAW SLAG AND FUSED SLAG

Oxide (wt. %)	Raw Slag	Fused Slag
CaO	42.9	21.8
SiO <sub>2</sub>	34.5	11.8
Al <sub>2</sub> O <sub>3</sub>	13.7	5.1
MgO	6.1	1.9
K <sub>2</sub> O	0.3	0.2
Fe <sub>2</sub> O <sub>3</sub>	0.6	0.7
SO <sub>3</sub>	1.1	0.1
Na <sub>2</sub> O		57.3

### B. Carbon Dioxide Immobilization

The schematic diagram of CO<sub>2</sub> immobilization used in this study is shown in Figure 1. For comparison with CO<sub>2</sub> immobilization methods, the following four conditions were examined in this study: (i) 200 mL of distilled water; (ii) 200 mL of distilled water with 1 g of fused slag; (iii) 200 mL of 0.08 M NaOH solution; and (iv) 200 mL of 0.08 M NaOH solution with 0.4 g of raw slag (the same amounts of NaOH and slag as those in fused slag used on (ii)). Two hundreds mL of distilled water or NaOH solution was put into the reactor (internal volume of 500 mL), and nitrogen gas was injected at a flow rate of 3 L/min until CO<sub>2</sub> concentration at the outlet of the reactor became lower than 100 ppm, measured by CO<sub>2</sub> meter (VAISALA, GM70T-C). Then, the temperature of the solution was kept at 20 °C using a heating system adapted to the reactor, and the solution was immediately stirred with mechanical agitation (250 rpm). The fused slag and raw slag were put into distilled water and NaOH solution, respectively, and CO<sub>2</sub> gas (1000 ppm in N<sub>2</sub>) was injected into the reactor at a flow rate of 5 L/min. The CO<sub>2</sub> concentration at the outlet of the reactor was continuously monitored by CO<sub>2</sub> meter until CO<sub>2</sub> concentration reached approximately 1000 ppm. After CO<sub>2</sub> immobilization experiment, the slurry was separated by filtration, and the concentrations of Ca, Si and Al in the filtrate were analyzed by inductively coupled plasma method (ICP) (Seiko, SII SPC400). The solid was dried in a drying oven overnight, and the mineralogical compositions of raw slag, fused slag, and these slags after CO<sub>2</sub> fixation were obtained by X-ray diffraction (XRD) (Rigaku, RINT-2500).



1: N<sub>2</sub> cylinder, 2: CO<sub>2</sub> cylinder (1000 ppm in N<sub>2</sub> gas), 3: Flowmeter, 4: Stirrer, 5: Thermometer, 6: Bubbler, 7: Stirred tank for gas absorption, 8: Water jacket, 9: Thermostatic bath, 10: Probe, 11: CO<sub>2</sub> concentration measurement

Fig. 1. Schematic diagram of CO<sub>2</sub> immobilization system.

### III. RESULTS AND DISCUSSION

CO<sub>2</sub> concentrations at the outlet of the reactor through (a) distilled water and (b) fused slag slurry were shown in Fig. 2. The CO<sub>2</sub> concentration through distilled water rapidly rises to around 1000 ppm within 30 min (Fig. 2 (a)), whereas that through fused slurry indicates the same tendency as that of distilled water until the CO<sub>2</sub> concentration rises to 600 ppm and thereafter CO<sub>2</sub> concentration gradually increases to around 1000 ppm for more than 3 hours (Fig. 2 (b)). It was confirmed that CO<sub>2</sub> was immobilized into the solution by adding fused slag to distilled water.

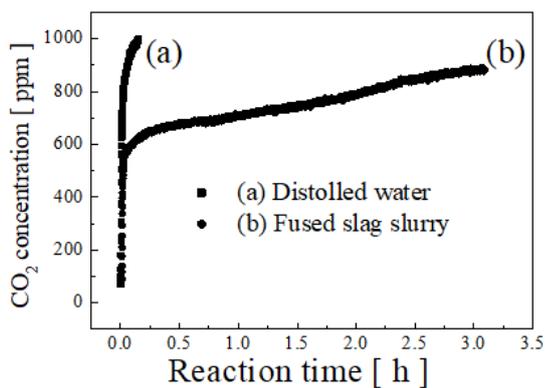


Fig. 2. CO<sub>2</sub> concentrations of the outlet of the reactor through (a) distilled water and (b) fused slag slurry.

XRD patterns of (a) raw slag, (b) fused slag and (c) fused slag after CO<sub>2</sub> immobilization experiment are shown in Fig. 3. The raw slag is an amorphous substance shown by a broad peak of 20 – 40 ° (Fig. 3 (a)), and it is turned into fused slag containing sodium

salts with high solubility by alkali fusion (Fig. 3 (b)). After injecting CO<sub>2</sub> into the fused slurry, the peaks of the sodium salts contained in the fused slag disappeared and those of calcite (CaCO<sub>3</sub>) appeared in the fused slag after CO<sub>2</sub> immobilization experiment (Fig. 3(c)).

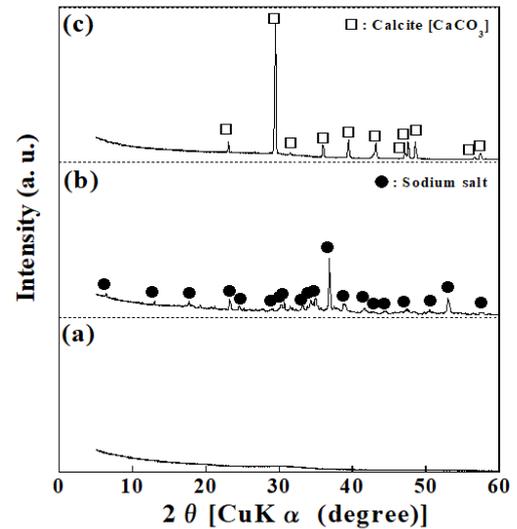


Fig. 3. XRD patterns of (a) raw slag, (b) fused slag and (c) fused slag after CO<sub>2</sub> immobilization experiment.

Next, the behavior of CO<sub>2</sub> immobilization using conventional method was investigated by adding raw slag powder to NaOH solution under the same conditions as using fused slag. CO<sub>2</sub> concentrations at the outlet of the reactor through (a) slag slurry and (b) NaOH solution are shown in Fig. 4. It was confirmed that almost same behaviors are exhibited when NaOH solution is used with and without BF slag addition. CO<sub>2</sub> concentration rises to 600 ppm within 30 min, and then gradually increases to 1000 ppm.

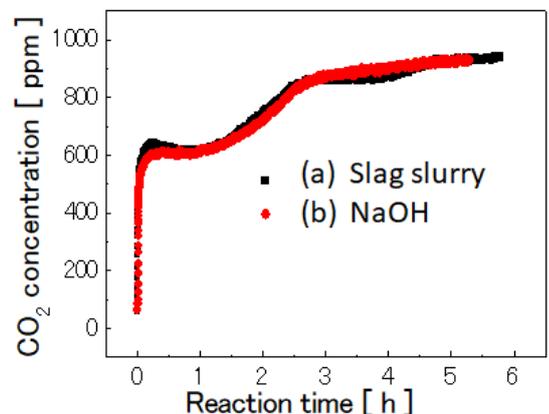


Fig. 4. CO<sub>2</sub> concentrations at the outlet of the reactor through (a) slag slurry and (b) NaOH solution.

XRD patterns of (a) raw slag, (b) raw slag after CO<sub>2</sub> immobilization experiment are shown in Fig. 5. A broad peak of 20 – 40° was confirmed in the raw slag, and only a slight peak of calcite was confirmed in the slag after the CO<sub>2</sub> immobilization experiment.

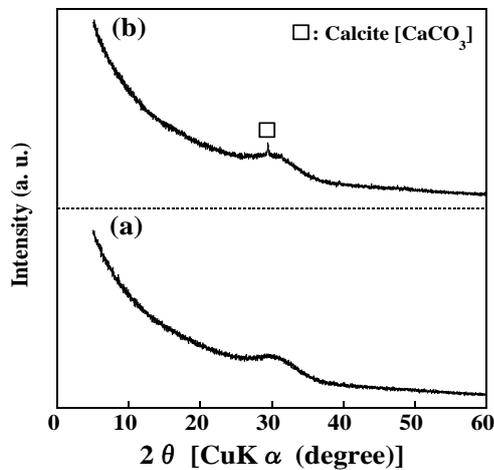


Fig. 5. XRD patterns of (a) raw slag and (b) raw slag after CO<sub>2</sub> immobilization experiment.

Concentrations of Ca, Si and Al in the solution after CO<sub>2</sub> fixation experiment are shown in Table 2. The Ca, which most contained in the raw slag, shows the lowest concentration, and the contents of Si and Al in the solution is higher than that of Ca. It is noted that pH of distilled water is neutral (5.8) and that with the fused slag addition after CO<sub>2</sub> immobilization experiment was alkaline (10.4).

TABLE II. CONCENTRATIONS OF CA, SI AND AL IN THE SOLUTION AFTER CO<sub>2</sub> IMMOBILIZATION EXPERIMENT

	Concentration (mg/L)		
	Ca	Si	Al
Fused slag	1.9	16.4	10.2
Raw slag	2.2	4.6	2.1

From these results, after adding fused slag to distilled water, the sodium salts dissolved into the solution to become an alkali solution, solution can dissolve CO<sub>2</sub> as carbonate ion or bi-carbonate ion, and Ca dissolved from the fused slag and these ions are reacted to be calcite. Therefore, it is thought that the rise of the CO<sub>2</sub> gas concentration at the outlet of the reactor is displayed as compared with the case of distilled water because CO<sub>2</sub> immobilization occurred after dissolving fused slag into distilled water.

Concentrations of Si and Al in the solution using raw slag are lower than those using fused slag, while that of Ca is almost same. It is noted that the pH of

NaOH solution is strongly alkaline (13.4), that of the solution without the slag addition after the experiment is 10.4, and that of the solution with the slag addition after the experiment is 10.3. These results indicate that CO<sub>2</sub> immobilization mainly depends on CO<sub>2</sub> absorption by NaOH solution and little immobilization reaction by the slag occurs.

From these results, it is considered that the CO<sub>2</sub> immobilization method using fused slag is an effective method because the CO<sub>2</sub> immobilization reaction (calcite formation reaction) occurs even at low temperature as compared with the conventional method.

#### IV. CONCLUSION

In this study, we attempted a new method for CO<sub>2</sub> immobilization using BF slag fused with NaOH. CO<sub>2</sub> can be immobilized effectively using the fused slag slurry as calcite, in comparison with the conventional method that can mainly immobilize CO<sub>2</sub> by absorption of NaOH solution with the formation of a little amount of calcite. These results indicate that CO<sub>2</sub> immobilization is effective using BF slag fused with NaOH in comparison with BF slag powder and NaOH solution.

From these results, it can be expected as an eco-process in the steelmaking process where it is possible to reduce carbon dioxide discharged in large quantities from the steelworks using by-product, BF slag, and unutilized energy in steelworks.

#### ACKNOWLEDGMENT

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