

Absorption of CO₂ in EAF Reducing Slag from Stainless Steel Making Process by Wet Grinding

B.M.N. Nik Hisyamudin, S. Yokoyama, and M. Umemoto

Abstract—In the current study, we have conducted an experimental investigation on the utilization of electric arc furnace (EAF) reducing slag for the absorption of CO₂ via wet grinding method. It was carried out by various grinding conditions. The slag was ground in the vibrating ball mill in the presence of CO₂ and pure water under ambient temperature. The reaction behavior was monitored with constant pressure method, and the changes of experimental system's volume as a function of grinding time were measured. It was found that the CO₂ absorption occurred as soon as the grinding started. The CO₂ absorption was significantly increased in the case of wet grinding compare to the dry grinding. Generally, the amount of CO₂ absorption increased as the amount of water, weight of slag and initial pressure increased. However, it was decreased when the amount of water exceeds 200ml and when smaller balls were used. The absorption of CO₂ occurred simultaneously with the start of the grinding and it stopped when the grinding was stopped. According to this research, the CO₂ reacted with the CaO inside the slag, forming CaCO₃.

Keywords— CO₂ absorption, EAF reducing slag, vibration ball mill, wet grinding.

I. INTRODUCTION

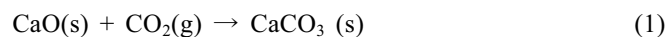
TREMENDOUS amount of fossil fuel had been used since the industrial revolution in the late of 18th century. The invention of the internal combustion engine and its use in automobiles and trucks greatly increased the demand for gasoline and diesel oil, both made from fossil fuels. However, this high consumption of fossil fuel was led to the harmful CO₂ gas emissions. About 21.3 billion tons of anthropogenic CO₂ was produced yearly, but it is estimated that natural processes can only absorb about half of that amount, so there is a net increase of 10.65 billion tones of atmospheric carbon dioxide per year [1]. This positive imbalance between the emission and absorption results in the continuing increase in atmospheric concentrations of CO₂ gas.

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In addressing this issue, several actions have been proposed to mitigate the global warming, such as the increase in the efficiency of energy conversion, energy savings, development of renewable carbon free energy sources (nuclear, solar, wind), and sequestration of anthropogenic CO₂ [2]-[5]. However, the fossil fuels including petroleum, natural gas and coal account for 86% of world energy demand for the current energy system [6]. The use of fossil fuels will likely continue at the next decades due to both its low cost and high availability. Thus, reduction of anthropogenic CO₂ is highly essential in order to recover and/or maintain the stability of nature.

The process of CO₂ absorption by the carbonation of industrial residue is a potentially attractive route for the CO₂ reduction that has received much attention in recent years [7]-[10]. The presence of CaO inside the substances accounts for the high potential of reaction between the slag and CO₂. The basic concept of the reaction is to transform the lime into carbonate as the following reaction:



The EAF reducing slag is a co-product of steelmaking processes. Typically, the EAF reducing slag production is about 70 kilograms per ton of steel produced. In Japan, about 1,538,880 tons of reducing slag was produced in 2007 and parts of it, about 124,740 tons, were not reused, and were sent to landfill for disposal [11]. Interest in using this material as sources of CO₂ absorption has arisen because they are readily available, and most often produced near emission sources of massive carbon dioxide. In previous research, the reactions of CO₂ with CaO and waste slag under dry and wet grinding were investigated [12]-[14]. Therefore, our present study is to investigate the effect of each experimental parameter on the absorption of CO₂ into EAF reducing slag.

II. EXPERIMENTS

A. Sample

EAF reducing slag from stainless steel making process was used in this study. It was mainly composed of particles with about <0.5 mm in size. Figure 1 shows the image of the slag before grinding. The chemical composition of the slag measured by energy dispersive X-ray (EDX) is shown in Table 1.



Fig. 1. Image of reducing slag before grinding

TABLE 1 CHEMICAL COMPOSITION OF REDUCING SLAG. [MASS%]

CaO	SiO ₂	Al ₂ O ₃	MgO	FeO	MnO	Cu O	Other s
63.4	19.0	3.7	3.9	2.3	1.7	1.8	4.4

B. Apparatus

The behavior of CO₂ absorption into the reducing slag was performed under wet grinding method. The schematic diagram of the experimental apparatus is shown in Figure 2. The apparatus was mainly composed of the vibration ball mill, the pressure sensor and gas volume meter. Frequency speed and amplitude of the vibration ball mill were 1200 rpm and 8 mm respectively. 180 pieces of alumina ball with 20 mm in diameter were used in the experiment. The volume of gas in the apparatus was measured by the gas volume meter that was equipped with a motor driven piston. The pressure in vessel was kept at the constant pressure of 101.3 ± 0.1 kPa during the experiment.

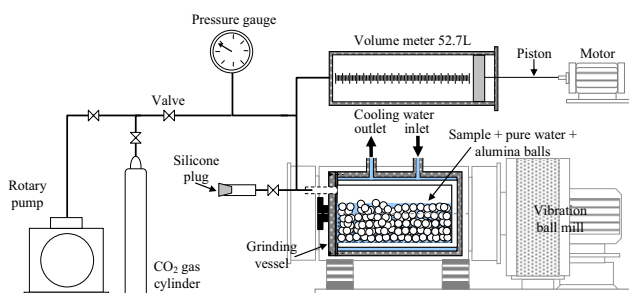


Fig. 2 Schematic diagram of experimental apparatus

C. Procedure

The slag and the alumina balls were placed in the grinding vessel. Then, the air inside the vessel was evacuated by a rotary pump. When the internal pressure was completely vacuumed, CO₂ gas was injected into the vessel until the inner pressure reached 1 atm. These steps were repeated two times to assure that all air inside the vessel was fully replaced by CO₂. Finally, the CO₂ gas was injected until the inner pressure reached the desired initial pressure. The pressure of CO₂ injected indicates the initial pressure of the system. After the replacement of CO₂ gas, the pure water was immediately injected into vessel under CO₂ flow. Subsequently, the grinding vessel was set on the

vibration ball mill and the grinding started. The experiment was conducted by change in the amount of water, amount of sample, diameter of alumina balls, initial pressure of CO₂ and initial particle size of slag. The details are as shown in Table 2.

The change in the volume was monitored and measured as a function of grinding time by the gas volume meter. The gas in the grinding system was sampled through the silicone plug by a micro syringe, and was analyzed by the gas chromatograph. The valve before the silicone plug was usually closed except for this purpose. The mineralogy characterization of the starting and the ground products was conducted by X-ray diffractometer (XRD) by the condition of Cu K α radiation beam ($\lambda=1.5406\text{\AA}$), 40kV, 30mA, scan speed of 2° per minute and ranging from 5° to 90°. The ground slag-water slurry was filtered by the centrifugal separator (1500 rpm, 5 min) to separate the solid and liquid products. The solid product was then dried in the dryer. The morphological structure of the solid product was characterized by scanning electron microscopy (SEM) equipped with energy dispersive X-ray (EDX) for the chemical composition analysis of solid material. The concentrations of Ca, Si, Al, Mg, Fe, Zn, Cr and Mn inside the liquid product were measured by inductively coupled plasma mass spectrometer (ICP-MS). The pH of the liquid product was also measured. Finally, the liquid product was dried in the oven for 1 hour at 150°C and the powder remained from the dried liquid product was characterized by XRD. The morphological structure was also observed by SEM.

TABLE 2 EXPERIMENTAL CONDITIONS

Parameters	Item/Value
Amount of water (ml)	0, 100, 200, 300, 400
Amount of slag (g)	0, 100, 200, 300, 400
Diameter of balls (mm)	0 (no balls), 2, 10, 20
Initial pressure (atm)	1, 2

III. RESULTS

A. CO₂ absorption by reducing slag during grinding process

Reaction between the CO₂ and the slag led to the reduction of gas pressure inside the grinding vessel. So, in order to fix the pressure at a constant value (≈ 101.325 kPa), the volume of the measuring system must be reduced. The volume reduction during the grinding is shown in Fig. 3. The amount of CO₂ absorption, n_{CO_2} (mol) was calculated based on ideal gas equation as shown below;

$$n_{CO_2} = \frac{P_{CO_2} \cdot \Delta V}{R \cdot T} \quad (2)$$

where P_{CO_2} is the CO₂ gas pressure inside the measuring system (≈ 101.325 kPa), ΔV (m³) is the amount of volume reduction shown in Fig. 3, R is the gas constant (8.3144 Pa·m³ / mol·K)

and T (K) is the room temperature.

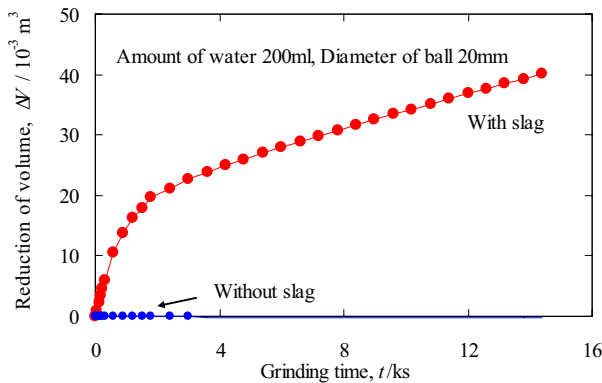


Fig. 3 Volume reduction during the grinding process

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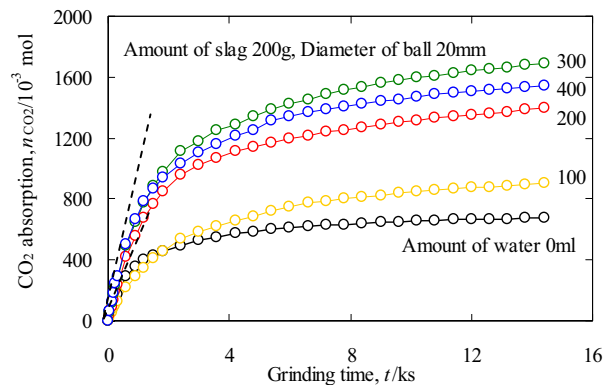


Fig. 4 Effects of amount of water on the CO₂ absorption

B. Effect of amount of water on CO₂ absorption

The effect of the amount of water on the CO₂ absorption is shown in Fig. 4. The dash line is referring to the gradient line of the absorption curve which indicates the initial absorption rate. The initial sorption rate was not significantly influenced by the amount of water. It was just increased slightly when more water used in the experiment. The rate was unchanged when water was more than 200 ml. On the other hand, the amount of CO₂ absorption at the end of the grinding was depended on the amount of water. It was increased as the amount of water increased. However, it started to decrease when water used was more than 300 ml. The amount of CO₂ absorption recorded the maximum value of about 1.7mol when 300 ml of water was used.

It can be noted that it took some time for the slag particles to be ground to finer particles. That explains why there was no significant change of the reaction rate in the early stage of the grinding even though the amount of water was increased. The CO₂ absorption started to change after 0.6 ks the grinding was begun. The amount of CO₂ absorption for the wet grinding was higher than that for the dry grinding. In this case, water acts as a lubricant that prevents the agglomeration of particles. The particles were agglomerated between each others in the case of dry grinding [14].

When too much water was used in the grinding vessel, the amount of CO₂ absorption was inversely decreased. In this case, water might act as a cushion and it mitigates the intensity of impact between alumina balls and the slag particles. Thus, it can be concluded that the amount of water gave a significant effect on the absorption of CO₂, but too much water was inversely led to the limitation of the absorption.

C. Effect of amount of slag on CO₂ absorption

Fig. 5 shows the effect of the amount of slag on the CO₂ absorption. Generally, the CO₂ absorption increased when the amount of slag increased. There was no significant change in the initial absorption rate for all cases. The retardation of CO₂ absorption was observed after certain time and it happened faster when lower amount of slag was used. When the amount

slag exceeded 200g, the CO₂ absorption for higher amount seemed to occur slowly after 1.5 ks. This might be due to the grindability factor where when more amount of slag was ground by the same number of alumina balls, the frequency of collision upon each particle would be decreased since the ball-to-slag ratio decreased. This was then reduced the number of particle's newborn surface that required for the CO₂ absorption. However, continuous grinding of the slag in higher amount prolonged the CO₂ absorption. The CO₂ absorption for 400g of slag was still increasing when the grinding was stopped at 14.4 ks.

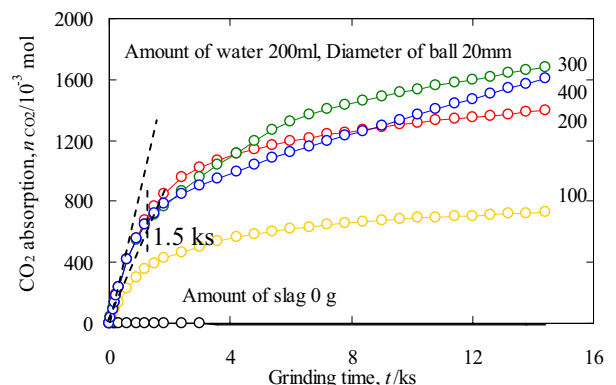


Fig. 5 Effects of amount of slag on the CO₂ absorption

D. Effect of diameter of ball on CO₂ absorption

The number of each ball was set as 180, 1450 and 181,000 pieces respectively, so that the total volume of the balls could be kept constant ($\approx 0.75L$). Result shown in Figure 6 indicates that the bigger balls show higher amount of CO₂ absorption than the smaller during the grinding. The amount of CO₂ absorption for 10mm and 20mm balls was almost same. The initial reaction rate was independent of the diameter of balls. Only a small amount of CO₂ absorbed when no ball used.

Collisions occurred inside the vessel during the grinding were between two balls and/or balls against the vessel wall and/or balls against the samples. Collision between the latter one might break the slag surface, producing a newborn surface of

the slag particle which then reacted with the CO₂. Collisions between the formers gave no effect on the absorption of CO₂. Increase in the number of balls may increase the possibility of the balls to hit each other and/or the vessel wall. In other words, the frequency of collision between balls and slags would be decreased when more balls were used. Furthermore, smaller balls also have smaller impact energy since the weight of it is lighter. That explains why smaller balls showed lower amount of CO₂ absorption.

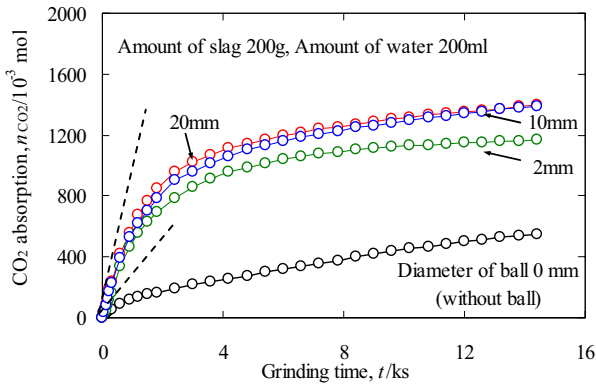


Fig. 6 Effect of diameter of ball on CO₂ absorption

E. Effect of initial pressure on CO₂ absorption

The initial absorption rate was not influenced by the initial pressure. However, the CO₂ absorption was depended on the initial pressure where it increased when the initial pressure was increased as shown in Fig. 7. The CO₂ absorption increased up to 1.6 mol when initial pressure was increased to 2 atm (202.65 kPa).

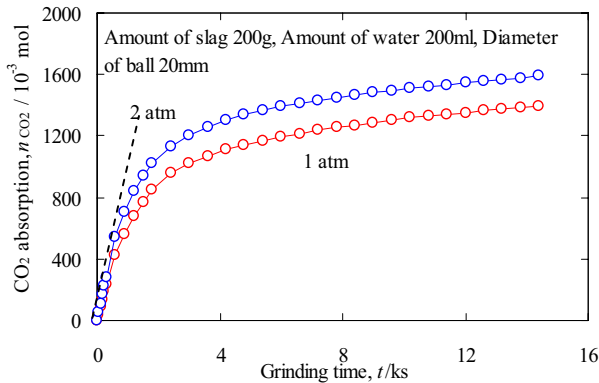


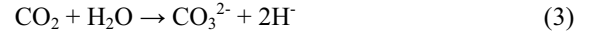
Fig. 7 Effect of initial pressure on the CO₂ absorption

F. XRD patterns of ground slag

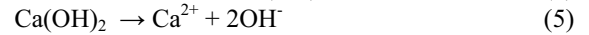
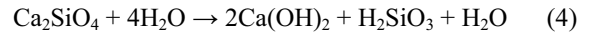
The starting sample was mainly composed of Ca₂SiO₄, MgSiO₂, and KAlSi₃O₈. These peaks were decreased as the grinding started, and were replaced by the peak of CaCO₃. As the grinding proceeded, the peak of CaCO₃ was increased.

It can be concluded that reactions occurred inside the grinding vessel were as follows;

- i. Dissolution of CO₂ into water



- ii. Dissolution of slag into water



- iii. Reaction between Ca²⁺ and CO₃²⁻



The water did not only promote the grindability of the slag, but also dissolved the slag and CO₂ for the reaction took place.

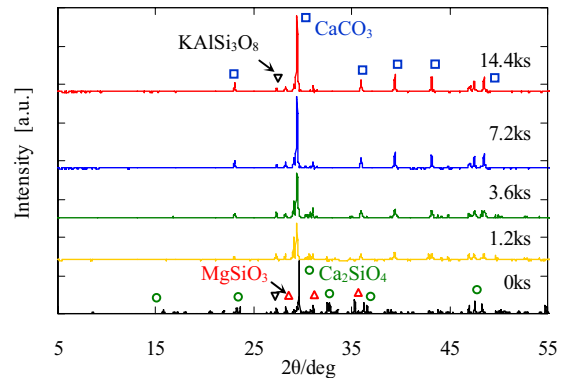


Fig. 8 XRD patterns of starting and ground slag

IV. CONCLUSION

The behavior of CO₂ absorption into EAF reducing slag discharged from the stainless steel making process via wet grinding method was investigated. It was found that the slag had a high potential of CO₂ absorption. The absorption of CO₂ into the slag was enhanced by the wet grinding method. This study was expected to contribute not only to the reduction of CO₂, but also to the effective utilization of unused slag as well as to the new application of EAF reducing slag.

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