

Utilization of EAF Reducing Slag from Stainless Steelmaking Process as a Sorbent for CO₂

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

Abstract—In this study, an experimental investigation was carried out to fix CO₂ into the electric arc furnace (EAF) reducing slag from stainless steelmaking process under wet grinding. The slag was ground by the vibrating ball mill with the CO₂ and pure water. The reaction behavior was monitored with constant pressure method, and the change of CO₂ volume in the experimental system with grinding time was measured. It was found that the CO₂ absorption occurred as soon as the grinding started. The CO₂ absorption under wet grinding was significantly larger than that under dry grinding. Generally, the amount of CO₂ absorption increased as the amount of water, the amount of slag, the diameter of alumina ball and the initial pressure of CO₂ increased. However, the initial absorption rate was scarcely influenced by the experimental conditions except for the initial CO₂ pressure. According to this research, the CO₂ reacted with the CaO inside the slag to form CaCO₃.

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

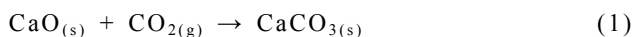
I. INTRODUCTION

TREMENDOUS amount of fossil fuels have been used since the industrial revolution in the late of 18th century. They have been burned to produce energy to run factories, business and so on. This high energy consumption has brought the human race a comfortable life. However, this combustion of a large amount of fossil fuels has led to the enormous emission of CO₂ gas which is one of the green house gases. About 21.3 billion tons of anthropogenic CO₂ is produced yearly, but it is estimated that natural processes can only absorb about half of that amount. Therefore, there is a net increase of 10.65 billion tones of atmospheric CO₂ per year [1]. This positive imbalance between the emission and the absorption results in the continuous increase in the atmospheric concentrations of CO₂ gas. In 2006, about 193 million ton of CO₂ gas was emitted from the steel industry in Japan. In order to solve this problem, the Japanese steel industry has established the “Voluntary

Action Program for Environmental Protection by Steelmakers”. Based on this action, the steel industry will reduce the energy consumption by 10% in comparison with that of 1990 level until fiscal year 2010. At the same time, they are also promoting the effective use of waste materials and by-products from steel industry.

Various methods and actions have been attempted and performed to deal with the global warming. Some of them are the increase in the efficiency of energy conversion and energy savings, the development of renewable carbon free energy sources (solar, wind etc) and so on [2]-[5]. However, the fossil fuels such as 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, the reduction of the anthropogenic CO₂ is highly required in order to recover and/or maintain the stability of nature.

The CO₂ absorption by the carbonation of industrial residue is a potentially attractive process for the CO₂ reduction. Such processes have been received much attention in recent years [7]-[10]. The presence of CaO in the substances is favourable for the carbonation. Thermodynamically, the following reaction can be easily occurred



The EAF reducing slag is a co-product of steelmaking processes. Typically, the production of EAF reducing slag is about 70 kg per ton of produced steel. In Japan, about 1,538,880 t of the reducing slag was produced in 2007. About 124,740 t of the slag was not reused, and was sent to landfill for disposal [11]. The EAF reducing slag is rich with CaO. Interest in using the slag as a sorbent of CO₂ has arisen because it is readily available and most often produced near the emission source of CO₂. In previous research, the reactions of CO₂ with CaO and waste slag under dry and wet grinding by a centrifugal and a vibration ball mill were investigated [12]-[14]. It was found that the wet grinding was superior to the dry grinding and so on. In this study, the absorption of CO₂ into EAF reducing slag from stainless steelmaking process was investigated. The effect of each experimental parameter on the absorption of CO₂ into EAF reducing slag was observed.

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II. EXPERIMENTS

A. Slag

EAF reducing slag which was discharged from stainless steelmaking process was used in this study. The slag which size was less than 5 mm was used in the experiment. Fig. 1 shows the image of the slag before grinding. The chemical composition of the slag measured by the energy dispersive X-ray (EDX) is shown in Table I.



Fig. 1 Image of the reducing slag before grinding

TABLE I
CHEMICAL COMPOSITION OF REDUCING SLAG

Compound	Composition (mass%)
CaO	45.7
SiO ₂	29.4
Al ₂ O ₃	9.6
MgO	5.6
P ₂ O ₅	2.7
Cr ₂ O ₃	1.2
CaS	2.3
MnO	0.5
FeO	0.5
NiO	0.6
CuO	0.7
ZnO	0.8
TiO ₂	0.4

B. Apparatus

The schematic diagram of the experimental apparatus is shown in Fig. 2. This apparatus is for measuring CO₂ with the constant pressure method. The apparatus was mainly composed of the vibration ball mill, the pressure sensor and the gas volume meter. The rotational speed and the amplitude of the vibration ball mill were 1200 rpm and 8 mm respectively. The grinding vessel that was lined with Al₂O₃ was water-cooled. The used balls were made of Al₂O₃. 180 pieces of alumina balls whose size were 20 mm were mainly used in the experiment. The volume of the 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 during the experiment.

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 less than 1.3 Pa, CO₂ gas was introduced into the vessel until the inner pressure reached 101.3 kPa. This vacume displacement was repeated twice to assure that all air in the vessel was fully replaced by CO₂. After the replacement of CO₂ gas, the pure water was poured into vessel under CO₂ flow. Finally, CO₂ gas was introduced until the inner pressure reached the predetermined pressure. Subsequently, the grinding was started.

Table II shows the details of the experimental conditions. The experiments were performed by changing the amount of water, the amount of slag, the diameter of alumina ball, and the initial pressure of CO₂.

The change in the gas volume was measured by the gas volume meter. The gas in the grinding system was sampled through the silicone plug by a micro syringe, and it was analyzed by a gas chromatograph that could detect H₂, O₂, N₂, CO, CO₂, CH₄, C₂H₄ and C₂H₆. The valve before the silicone plug was usually closed except for the gas sampling. The crystal structures of the slag before and after experiment were

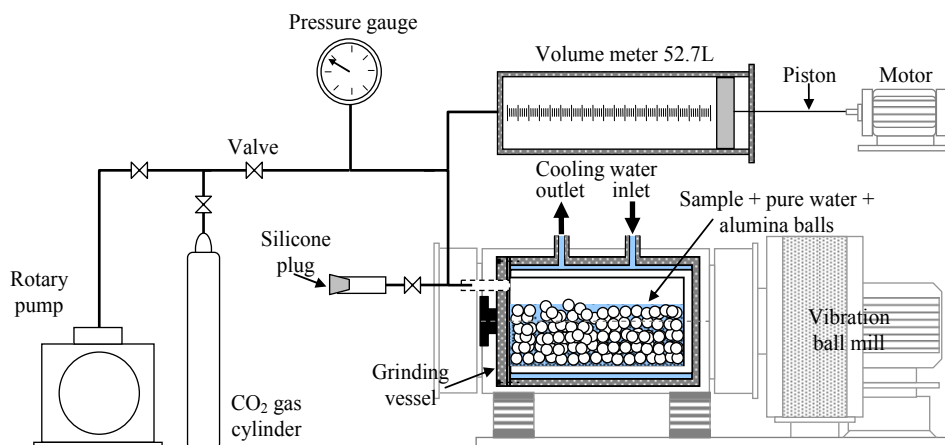


Fig. 2 Schematic of the experimental apparatus

measured by X-ray diffraction (XRD). The ground slag and the water after experiment were in slurry, and they were separated by a centrifugal separator. The remaining solid product was then placed in the dryer to totally remove the water from it.

TABLE II
EXPERIMENTAL CONDITIONS

Parameters	Item/Value
Amount of water [$\times 10^{-3}$ L]	0, 100, 200, 300, 400
Amount of slag [$\times 10^{-3}$ kg]	0, 100, 200, 300, 400
Diameter of alumina balls [mm]	2, 10, 20
Initial pressure [kPa]	101.3, 202.6

III. RESULTS

A. CO₂ Absorption by Reducing Slag during Grinding Process

Reaction between the CO₂ and the slag reduced the gas pressure in the grinding vessel. Therefore, in order to keep the pressure at a constant value, the volume of the measuring system must be reduced by moving the piston of the gas volume meter. The volume reduction during the grinding is shown in Fig. 3. The reduction of gas volume steeply increased at the early stage of the grinding. After that, it gradually increased. The amount of substance 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 in the measuring system [Pa], ΔV [m^3] is the amount of volume reduction, R is the gas constant [$8.3144 \text{ Pa}\cdot\text{m}^3 / \text{mol}\cdot\text{K}$] and T [K] is the gas temperature.

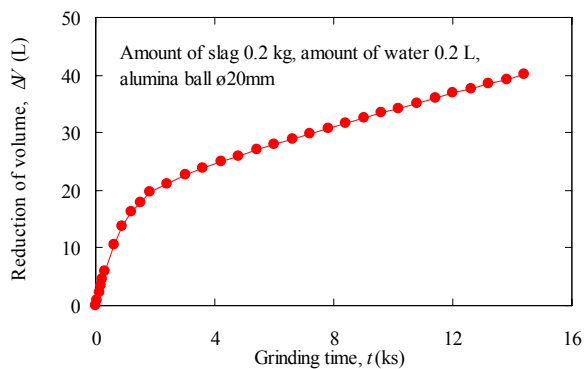


Fig. 3 Volume reduction during grinding

During the grinding, the gas temperature which was measured at outlet of the grinding vessel increased by about 6K. The expansion of the gas volume due to the temperature rise is only about 26 mL. This value is extremely small in comparison

with the reduction of the gas volume as shown in Fig. 3. Therefore, the effect of the temperature change on the change of the gas volume can be neglected. The analysis of the gas in the vessel by the gas chromatograph revealed that only CO₂ existed in the vessel. Consequently, the reduction of the gas volume is equivalent to the absorption of CO₂.

B. Effect of Amount of Water

The effect of the amount of water that was poured into the grinding vessel on the CO₂ absorption is shown in Fig. 4. Generally, CO₂ absorption rapidly occurred immediately after the grinding started, and then it gradually proceeded. Here, the behavior of CO₂ absorption in the case that the amount of water was 0 ml is the same as that under dry grinding. The amount of CO₂ absorption under the wet grinding was higher than that under the dry grinding. With regard to the CO₂ absorption, the wet grinding is superior to the dry grinding. The particles were agglomerated each others in the case of dry grinding [14]. It is thought that the water acts as a lubricant that prevents the agglomeration of the slag particles.

The initial sorption rate was not significantly influenced by the amount of water. On the other hand, the amount of CO₂ absorption at the end of the experiment was depended on the amount of water. Generally, it increased as the amount of water increased. The amount of CO₂ absorption reached the maximum value of about 1.7 mol when 0.3 L of water was used. However, it decreased when the water used was 0.4 L.

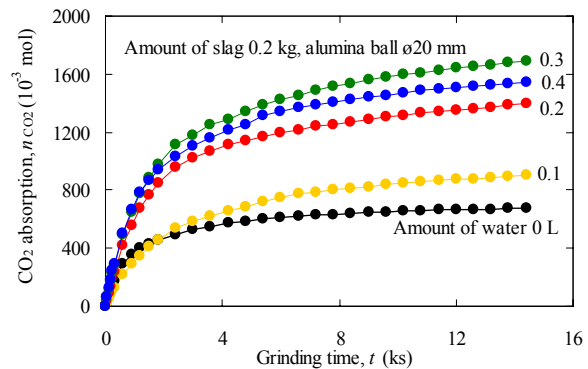


Fig. 4 Effects of amount of water on CO₂ absorption

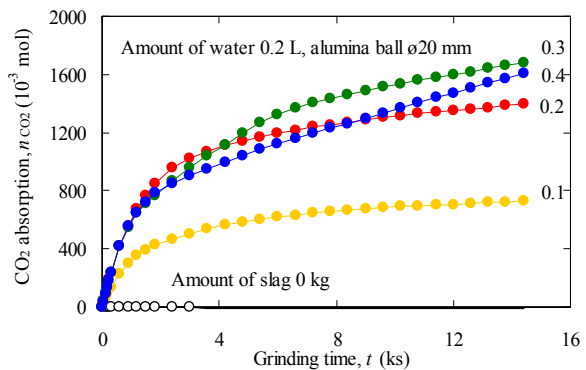


Fig. 5 Effect of amount of slag on CO₂ absorption

C. Effect of Amount of Slag

Fig. 5 shows the effect of the amount of slag on the CO₂ absorption. Generally, the CO₂ absorption increased with an increase in the amount of slag, but the amount of CO₂ absorption for 0.4 kg of weight of the slag was smaller than that for 0.3 kg of weight of the slag. The initial absorption rates were almost the same. Final amount of CO₂ absorption increased with an increase in the amount of the slag. Here, the CO₂ absorption in the condition that the amount of slag was 0 kg is the same as the CO₂ absorption in pure water. The amount of CO₂ absorption in water was very small.

D. Effect of Diameter of Alumina Ball

The numbers of each ball were set as 180, 1450 and 181,000 pieces respectively, so that the total volume of the balls should be constant ($\approx 0.75\text{L}$). Fig. 6 shows the effect of diameter of alumina balls on the CO₂ absorption. Generally, the amount of CO₂ absorption increased with an increase in the diameter of the alumina balls, but the amounts of CO₂ absorption for 10 mm and 20 mm balls were almost the same. The initial reaction rate was independent of the diameter of balls.

The slag was wet ground by collision between the balls-balls and between balls-vessel. The collision breaks the slag particle, and forms a newborn surface. The dissolution of the slag in the water was enhanced by the collision. In the case of using 2 mm of the ball in diameter, the impact energy which is given by the balls seems to be small in comparison with the energy by the relatively large balls. The space among the balls is small when the balls with 2 mm in diameter are used. Accordingly, the interfacial area between the CO₂ and the water is small. The amount of CO₂ absorption for the smallest ball became small because of the above mentioned reasons.

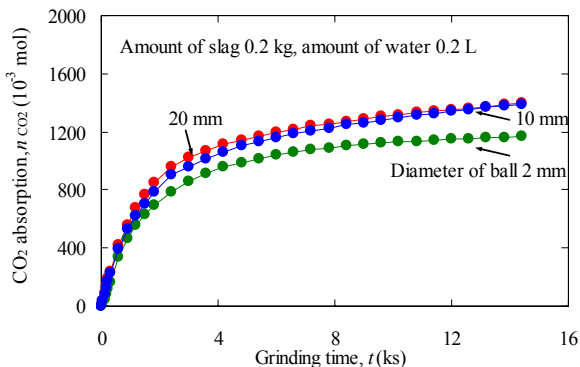


Fig. 6 Effect of diameter of ball on CO₂ absorption

E. Effect of Initial Pressure

Fig. 7 shows effect of the initial pressure of CO₂ on the CO₂ absorption. The initial absorption rate, as well as the amount of CO₂ absorption slightly increased with an increase in the initial pressure.

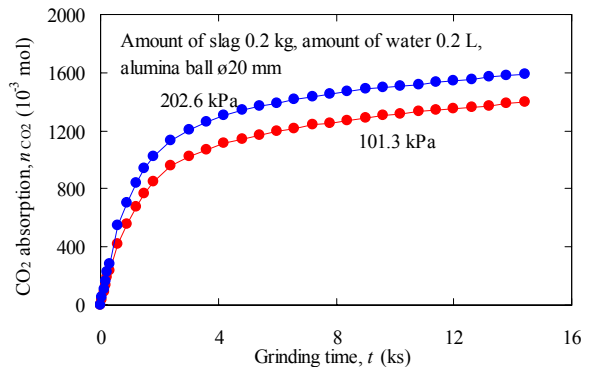


Fig. 7 Effect of initial pressure on CO₂ absorption

F. XRD Patterns of Ground Slag

Fig. 8 shows the XRD patterns of the slag before and after experiment. The slag before experiment is mainly composed of Ca₂SiO₄, MgSiO₂, and KAlSi₃O₈. These peaks were decreased as the grinding proceeded. The formation of CaCO₃ was identified, and the peak of CaCO₃ was increased as the grinding time increased.

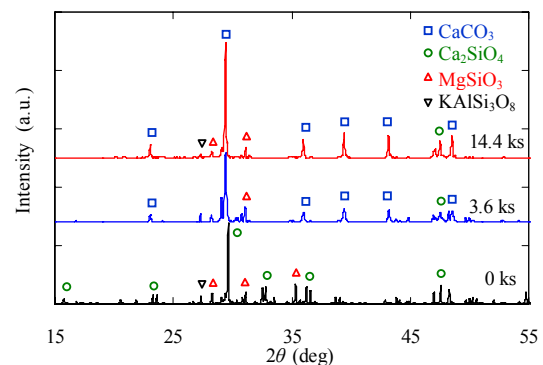


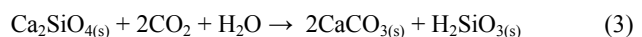
Fig. 8 XRD patterns of the slag before and after grinding

IV. DISCUSSIONS

A. Reaction Mechanism

The reaction under grinding is very complicated. The interfacial area between the slag and water may increase with the grinding time. It is also impossible to evaluate the interfacial area between the CO₂ and the water. Accordingly, the mechanism of the CO₂ absorption is considered qualitatively.

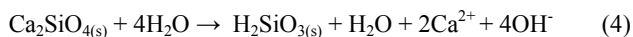
CaCO₃ was formed under the grinding. Then, the overall reaction of CO₂ absorption can be expressed as



Here, the subscript "s" indicates the solid phase. In the eq. (3), the formation of complex oxides and hydroxides, and the dissolution of SiO₂ are also put into consideration, but for the

reason of simplification, it is assumed that H_2SiO_3 forms during the grinding.

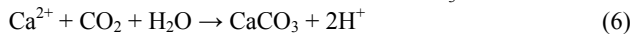
It is thought that the formation of CaCO_3 occurred at the following two sites; one is the interface between the slag and the water, and the other one is the interface between the water and the CO_2 . If CaCO_3 forms at the interface between the slag and the water, the formation rate of CaCO_3 , that is the rate of CO_2 absorption, may be influenced by the grinding conditions. However, the initial absorption rate of CO_2 was scarcely influenced by them, as shown in Fig. 4 and Fig. 5. Hence, it seems that the formation of CaCO_3 which is expressed by eq. (3) does not occur at the interface of the slag. Accordingly, the formation of CaCO_3 occurs at the interface between the water and the CO_2 . In this case, the overall reaction consists of the next three equations. One is the dissolution of the slag in water



Another one is the dissolution of CO_2 in water



The other is the formation reaction of CaCO_3



The reason for the initial absorption rate was not influenced by the grinding conditions was that the concentration of Ca^{2+} in eq. (6) was not affected by the grinding conditions due to there was enough amount of the slag in the vessel during the grinding process. The initial absorption rate increased with an increase in the partial pressure of CO_2 if the formation reaction of CaCO_3 occurs according to eq. (6).

B. Comparison of CO_2 Absorption

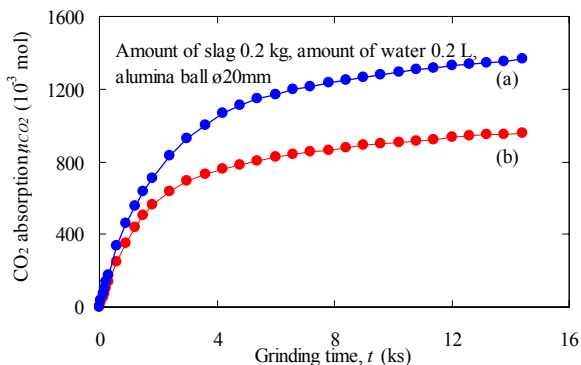


Fig. 9 Behavior of CO_2 absorption in different reducing slag which are discharged from stainless steelmaking process (a), and normal steelmaking process (b)

Fig. 9 shows the comparison between CO_2 absorption in the reducing slag used in this study and that in the reducing slag from normal steelmaking process [13]. The reducing slag which was discharged from the normal steelmaking process was mainly composed of CaO (50.1%), SiO_2 (21.0%), Al_2O_3

(18.6%), MgO (4.1%) and FeO (1.6%). Though the content of CaO in the reducing slag from normal steelmaking process is slightly higher than that in the reducing slag from stainless steelmaking process, the CO_2 absorption in the former was smaller than the latter. Al_2O_3 made it difficult for Ca in slag to dissolve into water. The content of Al_2O_3 inside the reducing slag from normal steelmaking process is about 2 times higher than that from stainless steelmaking process. Therefore, this explains why the CO_2 absorption in the normal steelmaking slag was lower than the stainless steelmaking slag.

V. CONCLUSION

The behavior of CO_2 absorption into EAF reducing slag discharged from the stainless steel making process under wet grinding method was investigated. The obtained main results are summarized as follows:

1. Amount of CO_2 absorption for wet grinding is significantly higher than the dry grinding. Because water prevents the agglomeration of particles during the grinding, the absorption of CO_2 into the reducing slag was enhanced by the wet grinding.
2. The initial absorption rate was independent on the amount of water, amount of slag and diameter of alumina ball. However, the absorption rate slightly increased with an increase in the initial pressure.
3. The amount of CO_2 absorption increased with an increase in the amount of water, the amount of slag, the diameter of alumina ball and the initial pressure of CO_2 . However, too much water was inversely led to the limitation of the absorption.
4. The CaCO_3 was formed during the grinding according to eq. (3) to (6). CO_2 could be fixed as CaCO_3 by this process.

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