Technical Report

Stabilization of Calcium Compounds in Steelmaking Slag

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Abstract

Steelmaking slag contains CaO, which generates a basic solution when in contact with water. For effective use, it is necessary to consider the alkali elution into the environment. Therefore, a basic experiment on carbonation treatment was conducted as a stabilization measure for Ca compounds to reduce the alkali elution. As a result, free lime in the steelmaking slag reacts selectively in the early carbonation reaction. It is suggested that the interfacial reaction based on the unreacted core model is the rate-determining step in the early stage of carbonation treatment, and after that, it is regulated by diffusion in the $CaCO_3$ product layer. In addition, the reaction rate is almost proportional to the pressure of CO_2, the higher apparent reaction rate constant is observed at a smaller particle size of steelmaking slag, but in accordance with the increase of particle size of steelmaking slag, the reaction rate constant which excludes the effect of particle size is increased. This result affirms that the reactivity of steelmaking slag with a bigger particle size is superior to that of steelmaking slag with a smaller particle size.

1. Introduction

In the refining process that removes impurities of hot iron metal, steelmaking slag that contains CaO as its major composition is produced. The steelmaking slag consists of oxides and contains CaO termed as free lime (hereinafter referred to as f-CaO). Although f-CaO becomes a problem for the effective use of the steelmaking slag in many cases, the steelmaking slag is used as the subbase course material for civil construction and cement clinker, and furthermore, is recycled in steelworks as a source of lime material. Thus most of the steelmaking slag produced is effectively utilized.

Since steelmaking slag solution exhibits a basicity of about pH 10–12.5 due to its main component of CaO, when using the steelmaking slag for effective utilization, attention should be paid to prevent the outflow of the elution (alkali elution) of high pH into the environment. The treatment to lower the pH of the steelmaking slag itself such as pH neutralization and/or insolubilization of Ca compounds are effective means in expanding the arena of effective usage of the steelmaking slag.

From such a viewpoint, we have continued to tackle the application development and the improvement of the product quality of Ca compounds, particularly f-CaO that influences the elution pH most significantly, taking an approach based on inorganic material engineering. This report describes the general slag treatment methods

and the content of the study on the carbonation treatment with CO_2. Since there are very few studies on the analysis based on kinetics, focusing on the reaction of f-CaO in particular, we have studied the reaction rate with respect to the carbonation of f-CaO contained in the steelmaking slag.

2. Effective Utilization and Treatment Method of Steelmaking Slag

The steelmaking slag resembles crushed stone in its appearance. The major composition of crushed natural stone is SiO_2 while that of steelmaking slag is CaO. Additionally, since steelmaking slag has a component close to that of Portland cement, steelmaking slag has hydraulicity, or hardens with water. In developing new usage, effective utilization has been pursued, taking into consideration the various characteristics of the steelmaking slag as described hereafter in addition to the abovementioned characteristics.

The steelmaking slag is used as subbase course material by taking advantage of its high strength, hydraulicity and high load bearing capacity, and as an aggregate of asphalt concrete owing to its high hardness and excellent abrasion resistance. In addition to the above, steelmaking slag is used as a soil improving material to substitute lime and the following blocks have been developed: hydrated solidified body[1–3] made by solidifying the mixture of the steelmak-

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ing slag and the fine-powdered blast furnace slag, and carbonated solidified body made by solidifying the steelmaking slag through a reaction with CO_2.[4, 5] In addition to the usage in the form of a block, as marine plants easily grow on such a material under sea, the blocks are crushed and utilized for growing marine forests and building fishing banks as broken stone substituting natural stone.[5, 6] Furthermore, there is a case in which the crushed block is mixed with the humic acid of humus soil and is utilized as a ferrous source that supplies ferrous ions stably to sea water to construct marine forests in the ruined shore area (the sea area covered with calcareous algae where no marine weeds grow).[7]

For such utilization, various treatments have been studied and are conducted for the steelmaking slag to be of a quality that fits the respective usage, the outline of which is described hereunder.

2.1 Aging treatment

Steelmaking slag contains f-CaO, which reacts with water in an environment and develops the hydration reaction as shown by Expression (1). Since the reaction accompanies volumetric expansion, which expands the slag itself and/or the slag-based construction body, problems are sometimes caused thereby.

$$CaO + H_2O \quad \rightarrow \quad Ca(OH)_2 \quad\quad (1)$$
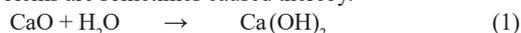
To suppress such expansion, a pretreatment termed as aging is conducted before shipment. This method accelerates the reaction of Expression (1) in advance and such aging treatments as follows are practically used: air aging treatment in which the hydration reaction is promoted for a period of time by rainfall or by the ambient moisture in the atmospheric air, accelerated aging treatments such as steam aging treatment with high temperature steam, hot water aging treatment with hot water and pressurized steam aging treatment.[7]

2.2 Solidification treatment

There are two solidification treatments: hydration solidification in which the fine-grained blast furnace slag and the steelmaking slag are kneaded and solidified, and carbonate solidification in which the steelmaking slag is solidified with $CaCO_3$ formed under a CO_2 gas atmosphere and acting as a binder.

In the former treatment, CaO-SiO_2-H_2O (C-S-H gel) and CaO-Al_2O_3-H_2O (C-A-H gel) are formed during the hardening reaction, during which process f-CaO is consumed and further, as the surface of the solidified body is densely covered by these products in gel-form, alkali elution is suppressed.[1]

It is reported that in the latter treatment, upon the manifestation of strength, minute $CaCO_3$ is precipitated in such a way that it covers the slag particles and glues the contacting particles together, forming blocks having significantly high strength.[8]

2.3 Carbonation treatment

Carbonation is the phenomenon of a reaction of CaO of the Ca compounds with CO_2 to form $CaCO_3$. Under a high temperature condition, CaO directly reacts with CO_2 as Expression (2), and at an ordinary temperature and under the existence of water, the reaction is promoted, following Expressions (3)–(5).

Under a high temperature condition,

$$CaO + CO_2 \quad \rightarrow \quad CaCO_3 \quad\quad (2)$$

At an ordinary temperature with water,

$$CaO + H_2O \quad \rightarrow \quad Ca^{2+} + 2OH^- \quad\quad (3)$$
$$CO_2 + H_2O \quad \rightarrow \quad CO_3^{2-} + 2H^+ \quad\quad (4)$$
$$Ca^{2+} + CO_3^{2-} \quad \rightarrow \quad CaCO_3 \quad\quad (5)$$
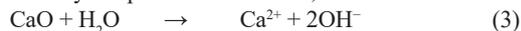
As $CaCO_3$ exists richly in nature in the forms of marble and/or lime tableland, $CaCO_3$ is a mineral of low solubility among Ca compounds. Therefore, by carbonating the soluble Ca compounds to insoluble $CaCO_3$, elution of Ca^{2+} is suppressed and the pH of the elu-

ent is lowered.

There are three major carbonation treatment methods: reaction of slag with CO_2 under a high temperature condition (dry method), blowing CO_2 to slag immersed in water (immersion method) and CO_2 ventilation through wetted slag (wetting method). Among them, the immersion method is most widely studied.

For instance, Lekakh et al.[9] state that the rate of carbonation is lower than that of Ca elution and that the reaction rate at the time is expressed by the limited rate of diffusion of CO_3 ions, and its apparent diffusion coefficient rapidly decreases along with the progress of carbonation.

Chang et al.[8] report that the rate of carbonation of the BOF slag, a type of steelmaking slag, is rate-limited by the diffusion rate of aqueous CO_2 within the product layer formed by the formation of $CaCO_3$ based on the shrinking core model.

Furthermore, Huigen et al.[10] report that, when slag is carbonated, a product layer of $CaCO_3$ is formed on the surface of the slag and the mineral substances of the SiO_2, CaO-SiO_2 and CaO-Fe_2O_3 system remain internally, and the pH is below ten (pH<10) when the carbonation ratio exceeds 60%.

Concerning the carbonation treatment by means of the wetting method under a low liquid-solid ratio condition, there are a number of reports about the neutralization in the field of concrete. For instance, Suzuki et al.[11] clarified that in the neutralization mechanism of C-S-H gel that is a mineral substance of cement, the larger the Ca/Si ratio, the lower the carbonation rate. Additionally, according to the report of Watanabe et al.[12], in the carbonation of a material of the cement system added with γ-Ca_2SiO_4, the carbonated depth decreases with the increase of CO_2 concentration and the void-sealing effect of the formed $CaCO_3$ increases.

With respect to the carbonation treatment of steelmaking slag, Tsutsumi et al.[13] have summarized the guidelines for various treatment conditions and showed that water is very important, and an optimum amount of water exists for the carbonation treatment of slag. As compared with the immersion method, in the wetting method, separation of the treated product from the process liquid and drying are not required. Since treatment tanks and the waste water treatment after treatment processing are not required, production with relatively simple plant equipment is possible.

3. Experiment of Carbonation

There are several reports on the study based on the kinetics of the carbonation reaction of Ca compounds of steelmaking slag. For example, it is reported that as the reactions of the CaO-SiO_2 phase and the CaO-Fe_2O_3 phase are slow as compared with that of $Ca(OH)_2$, even at the final stage, a considerable amount of such phases remain unreacted.[10] On the other hand, there are very few reports that focus on the reaction of f-CaO that plays a crucial role in the slag stabilization treatment. Then, with respect to the phase change of f-CaO in steelmaking slag along with the progress of carbonation reaction, the reaction mechanism was estimated, the influences of the slag particle size and the CO_2 pressure were studied and the behavior of the f-CaO in slag in the carbonation reaction was evaluated by using the unreacted core model.[14]

3.1 Experiment method

In **Table 1**, the result of the measurement of the major oxides contained in steelmaking slag by fluorescent X-ray analysis (ZSX Primus II of Rigaku Corporation) and in **Fig. 1**, the result of the measurement at an ordinary temperature of a slag test sample by X-ray diffraction (Ultima IV of Rigaku Corporation) are shown, re-

spectively. From these results, the existence of mineral phases of Ca compounds in steelmaking slag such as $Ca(OH)_2$, $CaCO_3$, Ca_2SiO_4, $CaFeSiO_4$, $Ca_2Fe_2O_5$, and FeO were confirmed.

3.2 Carbonation treatment

3.2.1 Carbonation treatment method

The apparatus for the carbonation treatment of steelmaking slag is shown in **Fig. 2**. A sealed vacuum desiccator (inner diameter 60 mm, inner volume 160 ml) having in its inside a beaker (inner volume 100 ml, made of stainless steel) containing a test sample and SUS balls (diameter 3 mm) was used as a carbonation reactor and the carbonation treatment was conducted by using this carbonation reactor.

Table 2 shows the experimental conditions. Since the carbonation reaction is an exothermic reaction, the amount of stainless steel balls was determined so as to keep the temperature rise to below 5 K. Furthermore, as for the optimum amount of water, in the preliminary experiment ahead of the main experiment, for a classified particle size, several test samples each of which is added with water of different amounts were carbonation-treated and the added water amount of the sample that showed the largest sample weight increase was taken as the optimum water amount.

The steelmaking slag was brought to an absolute dry condition at 383 K in a constant temperature oven and classified particle-size-

wise by a sieve. It was then provided for the carbonation experiment. The procedure of the carbonation treatment is shown in the following (1)–(5).

(1) Mix slag and pure water of a predetermined amount in the beaker and cover the beaker and leave it to rest for 30 minutes.

(2) Place inside of the vacuum desiccator the beaker with the stainless steel balls of a predetermined amount and seal the desiccator.

(3) Deaerate the carbonation reactor.

(4) Fill the carbonation reactor with CO_2. (filling timing is taken as $t=0$)

(5) Periodically measure the weight of the carbonation reactor and the inflow of CO_2 that replenishes the consumed CO_2.

3.2.2 Quantitative determination method after carbonation treatment

The slag after the carbonation treatment was absolute-dried at 383 K and was provided for various analysis tests.

The quantity of $CaCO_3$ in the slag test sample formed by carbonation treatment was measured with a thermogravimetric analysis apparatus (DTG-60/60H of Shimadzu Corporation), based on the weight reduction due to a decarboxylation reaction of $CaCO_3$ during 873–1 073 K when heated up to 1 273 K from an ambient temperature (temperature elevation rate: 10 K·min^{-1}) under a constant Ar flow. Furthermore, the quantities of CaO and $Ca(OH)_2$ were determined by the ethylene glycol extraction method and the value of CaO so determined added with the value of CaO deprived from $Ca(OH)_2$ was determined as f-Cao.

3.3 Result and study thereon

The amount of CO_2 absorbed by a unit weight of slag is defined as absorptance w. **Figure 3** shows the timewise change of w per particle size of steelmaking slag under a constant CO_2 pressure of 80 kPa. **Figure 4** shows the timewise change of w per CO_2 pressure for the steelmaking slag particle size of 0.212–0.325 mm.

Table 1 CaO, SiO$_2$, t-Fe and f-CaO compositions in steelmaking slag employed

Chemical composition	mass%
CaO	29.5
SiO$_2$	17.5
t-Fe	24.0
f-CaO	1.7
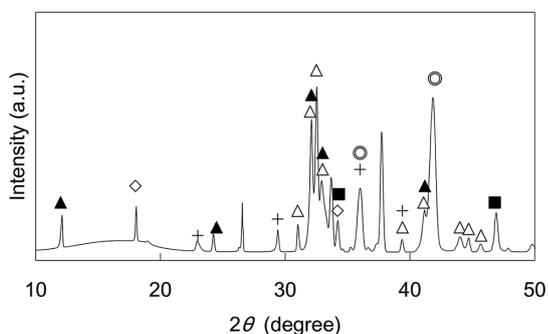
Fig. 1 X-ray diffraction pattern of steelmaking slag specimen before carbonation treatment
◇: Ca(OH)$_2$, ◎: FeO, +: CaCO$_3$, △: Ca$_2$SiO$_4$, ■: CaFeSiO$_4$, ▲: Ca$_2$Fe$_2$O$_5$
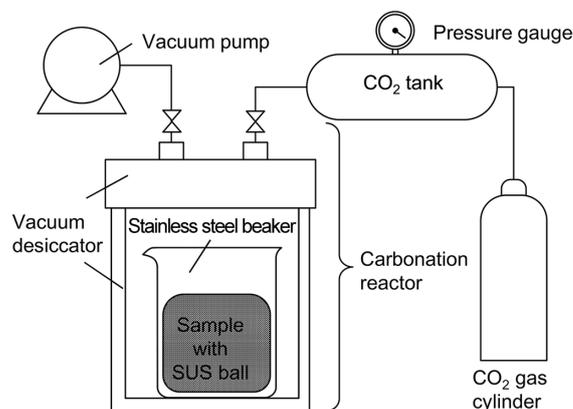
Fig. 2 Apparatus for carbonation treatment of steelmaking slag

Table 2 Experimental conditions of carbonation treatment of steelmaking slag specimen

Amount of slag	(g)	5.00						
Amount of stainless steel ball	(g)	400						
Temperature	(K)	298						
Time	(s)	4 800						
Particle size	(mm)	2.36–1.65	1.16–0.84	0.6–0.425	0.325–0.212			
Amount of water	(g)	0.10	0.15	0.20	0.40			
CO$_2$ pressure	(kPa)	80	80	80	10	20	40	80
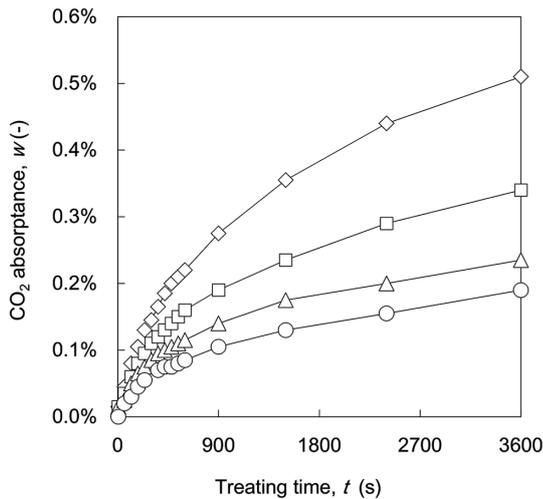
Fig. 3 Effect of particle size of steelmaking slag for CO_2 absorptance under 80 kPa in CO_2 pressure
◇: 0.212–0.325, □: 0.425–0.6, △: 0.84–1.16, ○: 1.65–2.36 (mm)

Fig. 5 Amount of CO_2 absorption and f-CaO reduction between raw and carbonated steelmaking slag for 1 500 s under 80 kPa in CO_2 pressure
■: CO_2 absorption, □: f-CaO reduction

Fig. 4 Effect of CO_2 pressure for CO_2 absorptance of 0.212–0.325 mm in particle size of steelmaking slag
◇: 10 kPa, □: 20 kPa, △: 40 kPa, ○: 80 kPa in CO_2 pressure

Since the weight of absorbed CO_2 calculated by the thermogravimetric analysis and the test sample weight change are almost equal as a result, the change in test sample weight was assumed to be due to the reaction with CO_2 and the CO_2 absorptance w was sought by Expression (6).

$$w = (W_t - W_{initial}) / W_{slag} \qquad (6)$$

where $W_{initial}$: the weight of the carbonation reactor after the deaeration (g), W_t: the weight of the carbonation reactor at the carbonating time of t (s) (g) and W_{slag}: the weight of the test sample before the experiment (g).

It was confirmed that the CO_2 absorptance w becomes larger as the particle size becomes smaller and the CO_2 pressure increases. Furthermore, under any condition, a rapid increase in w in the early stage is observed and the carbonation reaction progresses rapidly in the early stage of reaction.

Next, in **Fig. 5**, the amounts of CO_2 absorbed and the f-CaO re-

duction between before and after the carbonation treatment for 1 500 s under a CO_2 pressure of 80 kPa are shown.

Since the increase of the amount of CO_2 between before and after the carbonation treatment agrees for the most part with the amount of f-CaO reduced between before and after the carbonation treatment, it was confirmed that in the carbonation reaction at least up to 1 500 s, f-CaO of Ca compounds existing in steelmaking slag reacts on a priority base.

It was confirmed that this phenomenon takes place similarly under any CO_2 pressure condition. Then, assuming that f-CaO reacts selectively in the reaction up to 1 500 s, the reaction of f-Cao was studied using the unreacted core model.

Herein, the reaction ratio of f-CaO X was sought by Expression (7).

$$X = \frac{(W_t - W_{initial})/m_{CO_2}}{W_{slag} \cdot C_{f\text{-}CaO}/m_{CaO}} \qquad (7)$$

where m_{CO_2}, m_{CaO} are the molecular weight (g·mol⁻¹) of CO_2 and CaO, respectively and $C_{f\text{-}CaO}$ is the f-CaO concentration (mass%) in the steelmaking slag test sample before carbonation treatment.

The carbonation reaction of f-CaO in steelmaking slag was assumed to be a reaction based on the unreacted core model between water-dissolved CO_2 and f-CaO and the reaction rate was evaluated by using the unreacted core model expression of (8).[14] **Figures 6** and **7** show the result of plotting of F_1 vs. carbonation treatment time.

$$F_1 = 1 - (1 - X)^{\frac{1}{3}} \qquad (8)$$

In either result, F_1 in the early stage of the reaction shows a straight line with respect to the carbonation treatment time. As the CO_2 pressure rises, the linearity of the relationship is lost at a shorter carbonation treatment time. Furthermore, regarding the influence of the particle size shown in Fig. 7, under the condition of a CO_2 pressure of 80 kPa, disappearance of the linearity after 200 s–300 s is confirmed for any particle size. This is considered to be due to $CaCO_3$ formed by the carbonation reaction exerting influence on the microstructure of the slag. In the early stage of carbonation, f-CaO reacts and since the formation of an approximately equivalent
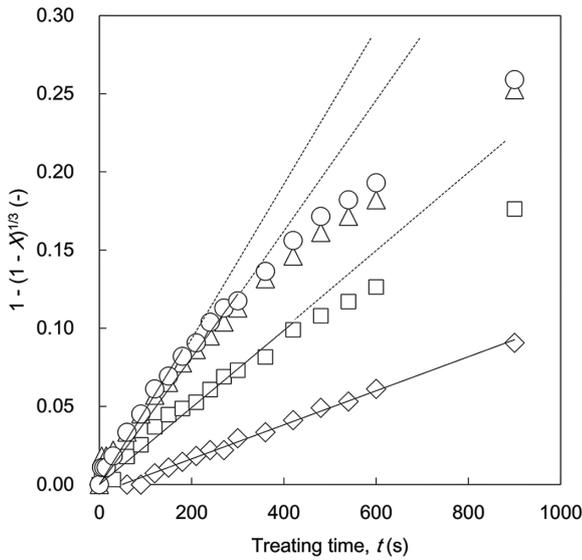
Fig. 6 F_1 plot for carbonation of 0.212–0.36 mm in particle size of steel-making slag
◇: 10 kPa, □: 20 kPa, △: 40 kPa, ○: 80 kPa in CO_2 pressure
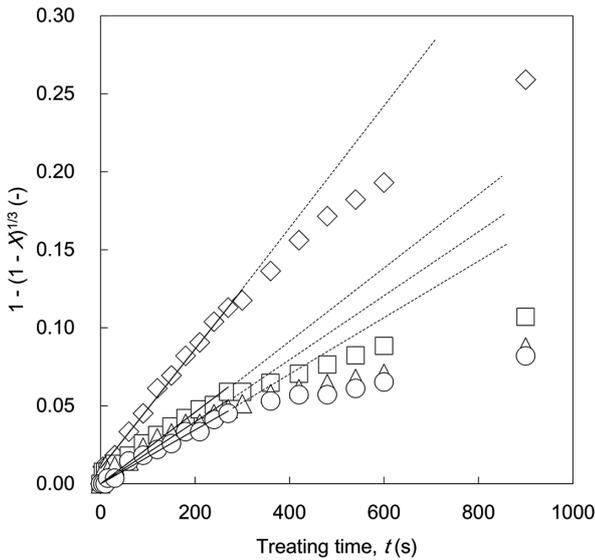
Fig. 7 F_1 plot for carbonation treatment under 80 kPa in CO_2 pressure
◇: 0.212–0.325, □: 0.425–0.6, △: 0.84–1.16, ○: 1.65–2.36 (mm)

amount of $CaCO_3$ is confirmed, the formation of the product layer of $CaCO_3$ formed by the carbonation reaction as shown by the Expressions (9)–(12) is considered, which is thought to be the resistance to the diffusion of dissolved CO_2 and/or Ca^{2+}.

$$Ca(OH)_2 \quad \rightarrow \quad Ca^{2+} + 2OH^- \qquad (9)$$
$$CO_2 + H_2O \quad \rightarrow \quad H_2CO_3 \qquad (10)$$
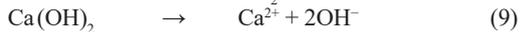
H_2CO_3 in Expression (10) dissociates based on Expression (11) under a high pH condition.

$$H_2CO_3 \quad \rightarrow \quad 2H^+ + CO_3^{2-} \qquad (11)$$

Ca^{2+} that eluted from the slag reacts with CO_3^{2-} formed by the CO_2 dissolved in water and $CaCO_3$ precipitates through a dissolution·precipitation reaction.

$$Ca^{2+} + CO_3^{2-} \quad \rightarrow \quad CaCO_3 \downarrow \qquad (12)$$

The aspect of the precipitation of this product layer of formed
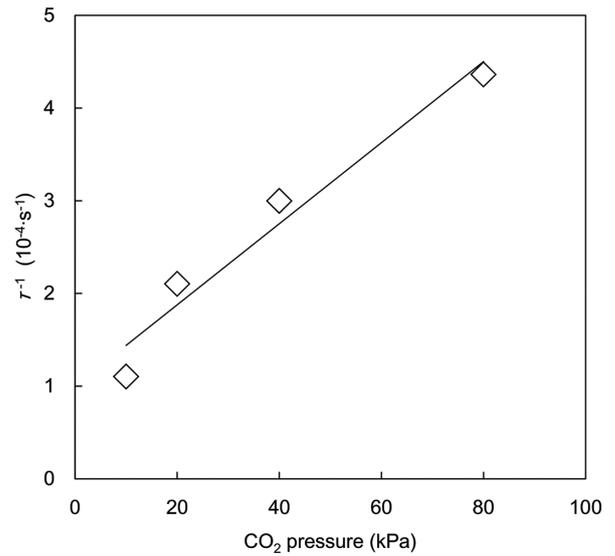
Fig. 8 Effect of CO_2 pressure for τ^{-1} of 0.212–0.325 mm in particle size of steelmaking slag

$CaCO_3$ is observed on the surface of steelmaking slag even in the carbonation by the immersion method of Zomeren et al.[15] In addition, Lekakh et al.[9] report that the product layer formed by carbonation treatment and elution becomes the resistance to the diffusion of Ca^{2+} and it is suggested that in the carbonation treatment in the wetting method of this experiment, the formed product layer similarly becomes the resistance to diffusion.

The inverse number (τ^{-1}) of the reaction completion time τ calculated from the inclination of the straight lines in Figs. 6 and 7 is considered as the apparent reaction rate of the carbonation reaction of f-CaO. Then, τ^{-1} under the respective CO_2 pressure condition was calculated and shown in **Fig. 8**.

In Expression (8), as F_1 is expressed as $t \cdot \tau^{-1}$, $\tau^{-1}(s^{-1})$ is expressed as Expression (13).[16]

$$\tau^{-1} = b \cdot C_A \cdot k_s \cdot \rho_B^{-1} \cdot R^{-1} \qquad (13)$$

where ρ_B: molar density of f-CaO (mol·m^{-3}), R: particle size (m), b: stoichiometric coefficient (-), C_A: CO_2 concentration in solution (mol·m^{-3}) and k_s: reaction rate constant (m·s^{-1}) per unit surface area.

Among them, ρ_B, k_s and b are assumed to be of constant values when the slag of an identical composition is used. With respect to the influence of CO_2 pressure on τ^{-1}, the increase of τ^{-1} along with the increase of the CO_2 pressure is witnessed and approximately in linear relation with CO_2. Since the solubility of CO_2 in water is approximately proportional to CO_2 pressure, the solubility of CO_2 in added water varies depending on the CO_2 pressure and is considered to influence τ^{-1}.

Following the above, regarding the influence of the particle size, assuming that C_A is a constant value under a condition of constant CO_2 pressure, the apparent reaction rate constant k' is expressed by Expression (14).

$$k' = \tau^{-1} \cdot R \ (= b \cdot C_A \cdot k_s \cdot \rho_B^{-1}) \qquad (14)$$

In **Fig. 9**, the result of the calculation of k' per respective slag particle size is shown. k' increases along with the increase of the slag particle size. From this, it was confirmed that, as compared with the steelmaking slag of small particle size, steelmaking slag having large particle size has higher reactivity per unit surface area obtained from the particle size. As the porosity of steelmaking slag is rela-
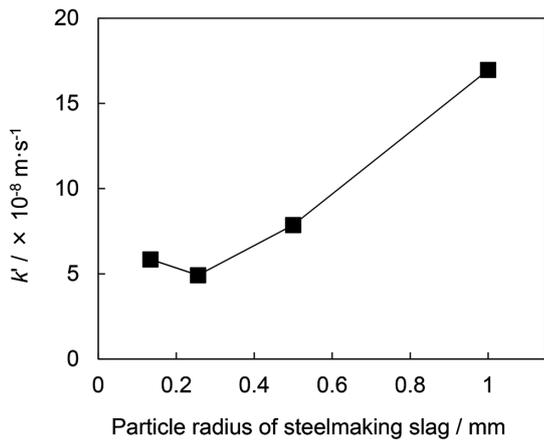
Fig. 9 Effect of particle size to k' under 80 kPa in CO_2 pressure

tively high and steelmaking slag has a wide pore size distribution, the larger the slag particle size, the larger the effective specific surface area becomes and therefore, higher reactivity is suggested.

4. Conclusion

In the carbonation treatment in the wet process method, in the early stage of carbonation, among the various Ca compounds existing in steelmaking slag, f-CaO was found to be selectively reactive. The carbonation of f-CaO in the early stage progresses with the rate-limit of the interfacial reaction based on the unreacted core model and the product layer of $CaCO_3$ formed by the carbonation reaction is suggested to be the resistance to the diffusion of dissolved CO_2 and Ca^{2+}.

Furthermore, the reaction rate is approximately proportional to the CO_2 pressure and although the apparent carbonation reaction rate constant is larger for the particles of a smaller size, the effective specific surface area is larger for the particles of larger size and higher reactivity is suggested.

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