Development of Rapid Stabilization Process for Steelmaking Slag

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Abstract

Fundamental experiments concerning about carbonation of steelmaking slag have been examined to solve the high pH water problem caused by alkaline contents from slag. We can find that slag carbonation reaction proceed easily at room temperature under the optimized conditions for additional water content to the slag, relative humidity of atmosphere and flow rate of gas containing CO_2 . And we can also confirm that slag carbonation will be finished in a few hours even in the full-scale experiments in the works.

1. Introduction

As one of the problems involved in promoting the usage of slag which occurs as a by-product of the steelmaking process, restraining the elution of highly alkaline water (the whitening of seawater) due to soluble lime (f-CaO), otherwise called free lime, contained in slag can be cited.¹⁾ Slag carbonation, which is a means of rendering f-CaO insoluble (harmless), has long been undertaken and there are many reports on the solidification of slag by carbonation.²⁻⁵⁾ However, the carbonation reaction itself (the reaction rate in particular) has seldom been discussed.^{6,7)}

Under such conditions, with the aim of building a practical process for efficiently stabilizing steelmaking slag, we reviewed the existing knowledge of slag carbonation and conducted basic experiments on the influence of various operational factors on the rate of carbonation reaction.^{8,9)} As a result, we were mostly able to clarify the reaction mechanisms. After that, through upscale experiments,¹⁰⁾ we have successfully established a new technology that permits carbonating slag in a short time even at room temperature.

2. Review of Existing Knowledge for Slag Carbonation

Concerning the carbonation of steelmaking slag, NKK (presently JFE Steel) reported in 1999 that they made a large block of slag called "marine block" by slag carbonation.²⁾ As for the solidification

of slag, however, several papers had been published before that. They include:

- Kondo et al.³⁾ of Tokyo Institute of Technology, who solidified converter slag by compression-forming slag-water mixture and curing it in a CO, atmosphere (1977).
- Haruna et al.⁴⁾ of Nippon Steel, who carbonated a mixture of fine particles of converter slag with water and studied the phenomenon whereby the mixture hardened (1979).
- Koyama et al.⁵ of NKK, who press-formed finely powdered converter slag in a wet state and hardened it using low concentration CO, (1980).

All these reports concerned the phenomena whereby converter slag is solidified by slag carbonation. Thus, technical discussions on the rate of the carbonation reaction have seldom been made.

In terms of studies on the rate of carbonation for substances other than slag from the steelmaking process, Shima, Daimon et al.⁶⁾ of Tokyo Institute of Technology published a report in 1989 on the rate of CO_2 absorption by hardened cement as measured from the standpoint of cement neutralization. Their study, however, focuses on the influence of the dryness of the specimens and the relative humidity of the atmosphere on the carbonation reaction; factors that govern the reaction rate were not considered.

Earlier, Matsuda, Yamada et al.⁷⁾ of the Government Industrial Research Institute of Kyushu, published a report in 1968 concerning the influence of water content and/or the relative humidity (RH) of

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the atmosphere on the rate of carbonation of slaked lime (Ca(OH)₂). In this report, the authors described some interesting results: when the water content was low (3%), the influence of RH on the carbonation rate was prevalent; when RH = 100%, the reaction rate was twice that at 80%, and 2 grams of Ca(OH)₂ were almost completely carbonated in 7 days; when water was added to Ca(OH)₂ under RH = 100%, the reaction rate increased; the carbonation rate was highest when the water content was in the region of 25%, in which case reaction time for carbonization decreased from 7 days to 3 days.

3. Experimental Method

As described above, it has been found that the carbonation reaction of slaked lime is influenced by the presence of contained water and the relative humidity of the atmosphere. Do these factors apply to the carbonation reaction of steelmaking slag as well? In this respect, we considered that if we could measure the change of slag weight continuously during the carbonation reaction process with the water content in slag and the relative humidity varied, it should be possible to determine which factors govern the slag carbonation reaction. Therefore, we first carried out a basic experiment using 100 grams of steelmaking slag to observe the behavior of the slag during carbonation. We then conducted upscale laboratory experiments using several kilograms of slag to try to clarify the mechanism of the carbonation reaction.

3.1 Basic experiment using 100 grams of slag

The experimental apparatus was made up of an acrylic chamber (30 cm \times 30 cm \times 50 cm) with a hole (10 mm diameter) in the upper wall and an electronic balance (AND GX-600) placed on top. An off-the-shelf funnel was fitted with a 100-mesh SUS sieve (45 mm across) at the bottom and hung from the electronic balance as the slag holder. Carbon dioxide gas (Class 1 available on the market) was passed through a flow meter, a couple of gas-washing bottles (1,000 ml each) filled with water, and a 10-liter gas reservoir. After the carbon dioxide was saturated with steam, it was fed into the acrylic chamber from the bottom. Two temperature and humidity sensors (T&D TD-72S) were installed inside the chamber, one at the top and the other at the bottom, so that the temperature and humidity, as well

as the slag weight, could be measured at the same time.

The relative humidity inside the chamber during the experiment was adjusted as required to meet certain conditions by mist spraying and feeding vapor-saturated carbon dioxide gas into the chamber at the start of the experiment. As for the temperature inside the chamber, the chamber interior was air-conditioned to maintain a basic fixed temperature (20). At certain experimental levels, the temperature was controlled using a drier capable of heating the atmosphere. The appearance of the experimental apparatus is shown in **Photo 1**.

Samples of steelmaking slag produced at certain steelworks of Nippon Steel and aged in the open air for about two months were collected, dried, classified and subjected to a composition analysis. The analysis results are shown in **Table 1**. Since it was found that a considerable proportion of f-CaO existed in a small lump of slag containing particles 1 mm or less in size, we decided to use mainly slag whose particle size was 1 mm or less which was considered to govern the elution of alkaline water from the standpoint of specific surface area (capacity coefficient).

100 grams of the slag were added with an arbitrary amount of water. After the slag was thoroughly mixed with water using a spatula, it was put in the funnel mentioned above. Then, an arbitrary volume of carbon dioxide saturated with steam was passed through the chamber and the change in slag weight caused by the carbonation reaction was measured. In addition, the amount of f-CaO in the slag after the reaction was measured.

3.2 Upscale experiments using several kilograms of slag

A cylindrical SUS basket with an inner diameter of 153 mm and 400 mm in height was put into a plastic outer cylinder with an inner diameter of 180 mm and 700 mm in height. 2 to 10 kg of slag with an arbitrary amount of water added was put in the SUS cylinder, and the whole apparatus was placed on an electronic balance. When putting the slag into the SUS cylinder, a temperature & humidity sensor (T&D TD-72S) was embedded in each of two points at different heights. As in the case described in 3.1, steam-saturated carbon dioxide (Class 1 available on the market) was fed into the SUS cylinder from the bottom of the outer plastic cylinder to start the slag



Photo 1 Summary of basic experimental apparatus



Photo 2 Summary of upscale experimental apparatus

	t-Fe	CaO	SiO ₂	MnO	MgO	P_2O_5	Cr_2O_3	Al_2O_3	t-S	f-CaO	C/S
-1mm	16.8	39.6	15.5	2.81	4.68	1.80	0.07	2.41	0.32	5.87	2.55
1-2.5mm	18.8	40.1	18.2	3.80	3.08	2.44	0.10	2.39	0.22	2.25	2.20
2.5-5mm	19.1	39.5	19.4	4.67	2.98	2.55	0.12	2.44	0.18	1.98	2.04
5-10mm	15.6	41.6	20.0	5.64	3.07	2.84	0.14	3.84	0.17	1.37	2.08
+10mm	13.5	45.2	18.4	5.84	5.91	1.86	0.15	2.45	0.14	4.79	2.46

Table 1 Analytical results of slag composition (%)

carbonation. The slag weight, temperature and relative humidity at different heights were monitored from time to time. The appearance of the experimental apparatus is shown in **Photo 2**.

In each of the experiments, since the f-CaO content of the slag was analytically known (see Table 1), the ratio of slag carbonation was calculated from the weight increase ΔW on the assumption that f-CaO eventually turned into CaCO₃.

Slag carbonation ratio (%)

 $= \Delta W / \{Amount of slag \times \% (f-CaO) \times 0.786 \times 100 \}$ (1)

Concerning the effect of f-CaO reduction in restraining the elution of alkaline water, it was measured according to the standard method for pH testing of soil suspensions employed by the Japanese Geotechnical Society.¹¹

4. Experimental Results and Considerations 4.1 Influence of various factors on carbonation reaction rate

(1) Influence of the relative humidity (RH) of the atmosphere $% \left({\left({R_{{\rm{T}}} \right)} \right)$

First, with the amount of water added to the slag and the flow rate of carbon dioxide kept constant at 20% and 0.5 l/min, respectively, the behavior of the slag being carbonated was studied with the RH inside the chamber varied. These results are shown in **Fig. 1**. It can be seen from Fig. 1 that when the RH is 100%, the carbonation ratio reaches 100% in 3 hours or so even at room temperature while when the RH is 80%, the carbonation ratio after 6 hours is less than half when the RH is 100%, as reported by Matsuda et al.⁷⁾ It should be noted that Fig. 1 shows carbonation rates higher than 100%. The reason for this phenomenon is probably that not only f-CaO but also f-MgO, etc. were carbonated in view of the fact that the f-CaO content of the slag after carbonation was not zero (0.9%).

(2) Influence of water amount added to slag

Next, with the RH of the atmosphere kept at 100%, the behavior of slag carbonation when the amount of water added to the slag (particle size: 1 mm or less) was varied from 0% to 30% (sprinkled over the slag) was studied. The study results are shown in **Fig. 2**. The behavior of carbonation of slag (particle size: 1 to 2.5 mm) when the amount of water added was varied from 0% to 10% is shown in **Fig. 3**. From these figures, it can be seen that when water is not added at all, the carbonation rate is almost zero, however with an increase in the amount of water added, the carbonation rate increases, and that the f-CaO content of the slag after carbonation decreases with the increase in carbonation ratio of the slag. On the other hand, in Fig. 2, for example, when the amount of water added is increased beyond 15%, the carbonation rate declines. Based on the results shown in Figs. 2 and 3 and the data obtained when the carbon dioxide flow rate was increased to 0.2 l/min, carbonation ratios for different



Fig. 1 Influence of relative humidity on slag carbonation



Fig. 2 Influence of additional water on slag carbonation-1



Fig. 3 Influence of additional water on slag carbonation-2



Fig. 4 Relationship between additional water and carbonation ratio after 3hours

amounts of water added after three hours were shown in **Fig. 4**. From this figure, it was found that there is an optimum amount of water to be added in the carbonation reaction, although it differs according to the slag particle size.

(3) Role of water added to slag in carbonation reaction

In order to determine whether water added to slag contributes to the hydration of CaO or to the carbonation reaction, we observed the behavior of carbonation with and without water added using the experimental apparatus and the same 100-mesh Ca(OH)₂ reagent as used by Matsuda et al. The observation results are shown in **Fig. 5**. When no water was added to the slag (line indicated by in Fig. 5), even Ca(OH)₂ which had been completely hydrated began gradually



Fig. 5 Influence of additional water on carbonation of Ca(OH),

absorbing water from the atmosphere, causing the slag carbonation ratio to increase sharply after a certain time. When water was added to the slag (line indicated by in Fig. 5), the carbonation reaction took place smoothly from the beginning. Thus, it was found that water was necessary not only for the hydration of slag, but also for the carbonation reaction itself. (In this figure, the difference in carbonation ratio between when wet CO₂ was used and when dry CO₂ was used is also shown. In either case, it is estimated that the steam contained in the CO₂ contributes to promotion of the carbonation reaction. The reason why the carbonation reaction almost stopped after the slag carbonation ratio reached around 80% is considered to be that the reagent had already been partly carbonated.)

(4) Consideration for slowdown of carbonation reaction with excess additional water

In order to clarify the reason why the carbonation reaction rate decreased when the amount of water added was increased, we observed the slag carbonation behavior (particle size: 1 mm or less) with 20% water addition, with which the carbonation rate was relatively high, and with a cover fitted to the bottom of the chamber to prevent carbon dioxide from flowing into the chamber. We also observed the carbonation behavior with the cover removed and with 30% water added, respectively. The observation results are shown in **Fig. 6**. It can be seen from this figure that while the carbonation rate decreases to only about half even when the reaction takes place only at the slag surface (CO₂ does not pass through into the slag), even this surface carbonation reaction does not take place when 30% water is added. Namely, the carbonation reaction is markedly impeded when there is an excessive amount of water around the slag and CO₂ does not pass through the slag. According to a previous study on the



Fig. 6 Behavior of carbonation of slag under several gas condition

neutralization of cement,⁴⁾ carbon dioxide is unable to penetrate a water-saturated sample all of whose micro-pores are filled with water, but the carbonation reaction proceeds as the sample dries. The results of the present experiment are considered to attest to the above carbonation behavior.

(5) Investigation of optimum amount of water to add for slag carbonation

Photo 3 shows two types of slag samples which were taken from the slag holder after being dried at 100 for 24 hours, one with 15% water added that was found to have the highest carbonation rate, and the other with 20% water (more precisely, it was later found to have a water content measurement of 22%) that produced a slightly lower carbonation rate (as shown in Fig. 2). From this photo, it was found that the sample with 20% water was coated in a CaCO, paste on the surface and formed into a compact mass, whereas the sample with 15% water was a loosely compacted mass from the surface of which slag particles easily came off when touched by hand. According to an earlier report,²⁾ the presence of capillary water in slag plays an important role in the formation of Marine Block. In light of the experimental conditions for slag whose particle size is 1 mm or less as used in the present experiment, even when the amount of water added is 20% or so, a water film (layer of free water) having a certain thickness is formed (locally) between slag particles. Even though this condition is not the same as the condition that was observed when 30% water was added (see Fig. 6), it is likely that the presence of free water impedes the carbonation rate to some degree.

In the casting of cement and/or monolithic refractory, the fluidity of the pasty powder is well known to be an important factor. Such fluidity is significantly influenced by the water added to and mixed with the powder. This water is roughly divided into boundary water (hydrated water and combined water) and free water, and the free water has to do with the fluidity. In order to allow quantitative evaluation for the ease of casting (the fluidity of paste), an index called "flow value" was regulated in JIS.¹²⁾ So, we considered that by using this index, it would be possible to assess the presence of free water in steelmaking slag when the amount of water added to the slag was varied. Therefore, we attempted to measure the tap-flow value of the slag. **Photo 4** shows the condition of the slag after it was vibrated by tapping.

As shown in Photo 4, with the addition of 10% water, the slag does not feel moist yet. When the amount of water added is increased to between 15% and 20%, the slag particles change to become black and wet and are gradually compacted into a mass. (The mass collapses even when it is only vibrated.) However, with 25% or more water added, the mass no longer collapses. With the increase in added water, the mass becomes fluid, showing the presence of free water



Photo 3 Influence of additional water on outlook of slag after carbonation

10% 15% 20% 30% 25% 35%

Photo 4 Influence of additional water on flow situation of slag



Fig. 7 Relationship between additional water and tap-flow value of slag

within. Fig. 7 shows the relationship between the tap-flow value (i.e. the expanse of slag mass after tapping) and the amount of water added. From this figure, it can be seen that in the case of the slag (particle size: 1 mm or less) used in the present experiment, the tap-flow value of the slag can be measured; that is, the presence of free water in the slag can be confirmed, when the amount of water added is 23% or more. This amount of added water agrees fairly well with the 20% water addition (precisely, 22%) that showed the presence of free water and allowed the slag particles to become compacted as shown in Photo 3.

In light of the result shown in Fig. 7 and the relationship between the carbonation rate and moisture content shown in Fig. 3, it is estimated that moisture content 8 to 10 percentage points less than the moisture content at which free water begins to appear represents the optimum range of water addition for efficient carbonation without causing slag particles to become compacted. Actually, the porosity and particle size distribution differ from one type of slag to another. Therefore, we consider that the optimum amount of water to be added for carbonation for a particular type of slag can be determined by the above tap-flow test (concrete slump test when the slag contains coarse particles)¹³⁾ in order to grasp the state under which free water appears in the slag.

(6) Influence of gas flow rate on carbonation rate

Fig. 8 shows the carbonation behavior of slag (particle size: 1 mm or less) when the flow rate of carbon dioxide was varied with the amount of added water kept at 15%. It can be seen from this figure that as the flow rate is increased from 0.1 l/min up to 0.5 l/ min, the rate of carbonation continues increasing. However, when the gas flow rate is further increased to 0.75 l/min or 0.9 l/min, the carbonation rate increases initially but slows down halfway. In this case, the ultimate carbonation ratio of the slag is not necessarily higher



NIPPON STEEL TECHNICAL REPORT No. 98 JULY 2008

0 0 60 120 180 time (min.) Fig. 8 Influence of gas flow rate on slag carbonation

than when the gas flow rate is lower. In the experiment, it was found that with the progress of the carbonation reaction, the temperature of the atmosphere inside the chamber rose. In addition, when the gas flow rate was 0.75 l/min or more, it was observed that surface of the carbonated slag dried out.

Since there was concern that increasing the gas flow rate would cause the slag to dry out, nitrogen was passed through the chamber in place of carbon dioxide and the resulting change in slag weight was measured. As a result, it was confirmed that when the flow rate of nitrogen was within 0.75 l/min, there was no loss in slag weight. Rather, there was a tendency for the slag weight to increase as any water was transferred from the water-saturated nitrogen gas to the slag. Thus, the flow of nitrogen gas did not cause the slag to dry. From the above facts, it is estimated that when the flow rate of carbon dioxide is 0.75 l/min or more, the heat generated by the rapid carbonation reaction in the early stages causes the temperature in the chamber to rise and the surface of the slag to dry, whereupon the supply of carbon dioxide ions to the slag via the wet phase near the slag surface is cut off and the carbonation reaction slows down.

(7) Influence of temperature on carbonation rate

As described in the preceding section, it was confirmed that with the increase in gas flow rate, the temperature of the atmosphere inside the chamber rose due to the heat generated by the carbonation reaction. Then, with the aim of grasping the influence of atmospheric temperature on slag carbonation, we carried out an experiment in which the temperature of the atmosphere in the chamber was varied from the beginning. The carbonation behavior observed during this experiment is shown in Fig. 9. As shown in the figure, an interesting result was obtained from the experiment. Namely, unlike the results of the series of experiments carried out at room temperature (20), the carbonation reaction slowed down as the atmospheric temperature was raised to between 40 and 60 , whereas the carbonation reaction continued smoothly at lower atmospheric temperatures.

In the inset in the top, left corner of Fig. 9, the RH values at the three different temperatures (20, 40, 60) in steady state are shown. Even though the experiment started at 100% RH in the chamber, the steam-saturated condition could not be maintained for long because the RH gradually decreased as the atmospheric temperature was increased. In view of the fact that the carbonation reaction is significantly influenced by the RH as shown in Fig. 1, it is undeniable that the experimental results shown in Fig. 9 are the combined effect of temperature and RH.

Nevertheless, from the relationship between the solubility of carbon dioxide in water and the atmospheric temperature shown in Fig.





Fig. 10 Relation between temperature and solubility of CO₂ in water

10,¹⁴⁾ it is a well-known fact that carbon dioxide dissolves in water more easily at lower temperatures. In view of the fact that: (1) the lower the temperature, the more active is the supply of carbon dioxide ions (the driving force for the carbonation reaction) to the slag via the wet phase of the slag, (2) the carbonation reaction is in itself an exothermic reaction which progresses faster at lower temperatures, and (3) as already mentioned, the saturated RH condition of the gas supplied and chamber atmosphere is easier to maintain at lower temperatures, the carbonation reaction of steelmaking slag is considered an interesting one which progresses smoothly even at normal temperatures, or rather more smoothly at room temperature.

4.2 Mechanism of carbonation reaction

From the results of the experiments to clarify the influence of various factors on the carbonation reaction of slag, it is evident that the addition of water to the slag promotes the carbonation reaction. It is estimated that this reaction, via the slag hydration process, undergoes the following processes almost concurrently.^{2, 7)}

$CaO + H_2O$	Ca(OH) ₂	(2)
Ca(OH),	$Ca^{2+} + 2OH^{-}$	(3)
$CO_2 + H_2O$	$2H^{+} + CO_{3}^{2}$	(4)
$Ca^{2+} + CO_3^{2-}$	CaCO ₃ (s)	(5)

Carbonated slag was embedded in resin and its cross section was ground to measure the distributions of various elements in the slag using E.P.M.A. The measurement results are shown in **Photo 5**. It was found that carbon (blue) exists in the part where the Ca-Si-O phase is considered to have been wet, that the water-soluble Ca has been carbonated, and that more porous slag has been wetted deeper inside, showing that carbon is distributed over almost the entire surface.

The important findings from the above observation results and the reaction mechanism are that: 1) the dispersion of material in the water phase that exists inside the slag is faster than that in the solid phase and the carbonation reaction between Ca ions and carbon dioxide ions in the water phase is promoted even at room temperature, and 2) the water phase must always exist because the carbonation reaction is an exothermic one, and that the steam contained in the chamber atmosphere and carbon dioxide plays a part in the supply of moisture to the slag.^{6,7} In other words, the points (necessary or optimum conditions) for speedy and sustainable carbonation of steelmaking slag at room temperature can be summarized as follows.

- (1) Securing a water phase (reaction site) and smooth supply of carbon dioxide Moisture control to prevent the occurrence of free water between slag particles
- (2) Restraining the water phase from becoming deficient due to the heat generated by the carbonation reaction and supplying water to the slag as required Securing the optimum gas flow rate and sufficiently high relative humidity
- (3) Maintaining a high carbon dioxide ion concentration in water and a high relative humidity Restraining the temperature rising during reaction (temperatures of the atmosphere and carbon dioxide itself)

4.3 Effect of restraining alkaline elution by slag carbonation

In order to grasp the behavior of alkali elution from carbonated slag, 10 grams of each slag sample that had been carbonated with



Photo 5 Distribution of each element in a section of slag particle (E.P.M.A.)

different amounts of water added (as shown in Fig. 2) were left immersed in 50 ml of seawater for six hours. The conditions of the seawater are shown in **Photo 6**. As shown in the photo, when the amount of water added was 10% or 20%, the seawater did not turn white. In the other cases, the seawater turned white.

With the aim of grasping the conditions under which seawater turns white, slag samples containing different amounts of f-CaO, including carbonated slag samples, were immersed in seawater to examine the correlation of the content of f-CaO, the pH value of seawater and the whitening of seawater. The examination results are shown in **Fig. 11**. It can be seen from this figure that when the pH value of seawater is about 9.5 or more, the seawater turns white. The relationship between the pH of seawater and the amounts of various ions dissolved in seawater is shown in **Fig. 12**.¹⁵ The reason for the



Photo 6 Influence of carbonation for slag on whitening of sea water



Fig. 11 Relationship between f-CaO contents and pH in sea water



Fig. 12 Relationship between pH value and content of several ion in sea water



Fig. 13 Behavior of alkaline elution from several slag

above phenomenon is probably that when the seawater has a pH value of 9.5 or more, the solubility of Mg^{2+} ions in seawater decreases and as a result, some of those ions precipitate in the form of $Mg(OH)_{2+}$.

Fig. 13 shows the relationship between elapsed time and pH value, obtained by immersing slag samples with and without carbonation and a reference granulated blast furnace slag sample under a more severe 3:1 liquid to solid ratio. The amount of alkaline elution from the carbonated slag was nearly the same as that from the granulated blast furnace slag. Even after 96 hours had elapsed, the pH value of the seawater remained at 9.5 or less. Thus, it was confirmed that in the case of carbonated slag, the whitening of seawater could be restrained satisfactorily.

4.4 Study for the required reaction time from upscale experiments

As described in the preceding sections, we could grasp by the theory of equilibrium that the slag carbonation reaction proceeds smoothly even at room temperature. Generally speaking, with the increase in scale of a particular chemical reaction, the time required for the reaction to be completed increases as well. Therefore, with the aim of quantifying the degree of increase of the carbonation reaction time with the increase in scale of the reaction and in view of the suggestion that with the method used for the small-scale experiment (the gas was let into the chamber from the bottom), it would be impossible to know exactly how much gas flows to the slag in the chamber, we carried out an upscale experiment on the carbonation of several kilograms of slag using a setup which ensures that all of the gas which is allowed into the chamber passes through the slag



Fig. 14 Image of gas flow under several experimental apparatus

being carbonated as shown in Fig. 14.

(1) Influence of amount of water added and flow rate of gas on carbonation rate

First, two samples of fine-particle slag (particle size: 1 to 5 mm), one weighing 2 kg and the other weighing 4 kg, were carbonated with the amount of additional water and the gas flow rate varied in the same way as in the small-scale experiment. The time-serial changes in carbonation ratio of the two samples are shown in **Figs. 15 and 16**. It can be seen from Fig. 15 that in the case of the 2-kg slag sample, when an excessive amount of water (7.5%) is added, the initial carbonation rate slows down. On the other hand, from Fig. 16, it can be seen that in the case with the optimum amount of water added (5%), the carbonation rate increases with the increase in the flow rate of carbon dioxide, but that when the gas flow rate is excessive, the carbonation reaction begins to slow down halfway. These and other phenomena in the upscale experiment are similar to those observed in the basic (small-scale) experiment.

In the basic experiment using 100 grams of slag, it took about 120 minutes for the carbonation reaction to be almost completed. In the upscale experiment, despite the fact that the amount of slag was more than 20 times larger than that used in the basic experiment, the carbonation reaction was completed in about 40 minutes. Thus, it was found that in the upscale experiment the carbonation of slag took much less time.

Fig. 17 shows examples of time-serial changes of temperature and relative humidity measured by sensors installed at two different points in the chamber at different slag heights during the upscale experiment. From the figure, it can be seen that about 10 minutes



Fig. 15 Influence of additional water on slag carbonation



Fig. 16 Influence of gas flow rate on slag carbonation



Fig. 17 Behavior of temperature and RH during carbonation (2kg)

after the experiment started, the gas reached the sensor installed at a point about 80 mm above the chamber bottom and carbonation of slag in the region of the sensor began, and that the heat generated by the carbonation reaction caused the atmospheric temperature to rise and the relative humidity to decrease temporarily and then increase again (at the end of the carbonation reaction). About 25 minutes later, exactly the same carbonation behavior was observed near another sensor installed at a point 140 mm above the chamber bottom. Thus, it was found that the area of carbonation shifts as the gas gradually rises through the slag layer, and that a partial carbonation reaction of a certain portion of the slag takes place quickly in about 15 minutes.

(2) Carbon dioxide flow rate (specific consumption) required for carbonation reaction

In the basic experiment using 100 grams of slag, a container filled with slag was hung from the top of a chamber and carbon dioxide was allowed into the chamber from the bottom. With this setup, it was impossible to know how much gas was flowing through the slag in the container. In the present experiment, as in the basic experiment, the phenomenon whereby the carbonation reaction slowed down with the increase in gas flow rate was observed as shown in Fig. 16. The specific consumption of carbon dioxide under the conditions in Fig. 16 was about 60 Nm³/t-slag at most, and the mass balance calculated from the reduction of f-CaO in the slag showed that the efficiency of carbon dioxide utilization was as low as about 50%. Therefore, we carried out another experiment using 10 kg of unsorted slag having a particle size distribution of 0 to 25 mm. The time-serial changes in temperature and relative humidity measured at different slag heights in the experiment are shown in **Fig. 18**.

The carbonation reaction behavior in which carbon dioxide slowly rises through the slag layer can be observed in Fig. 18. This behavior is considered to be due to the fact that the slag contained very fine particles and that the static pressure increased in proportion to the increase in the amount of slag. It was found that as long as the apparent gas ascension rate was 8 to 10 mm/min, the reaction zone moved from the lower part of the slag layer upward and the carbonation reaction was almost completed in about an hour even when the amount of slag was increased to 10 kg.

In other words, since the basic reaction involved in the carbonation mechanism is a gas-liquid reaction between Ca ions and carbon dioxide ions within the water phase contained in the slag, as long as the condition under which wet slag and carbon dioxide make contact with each other efficiently at the interface of the reaction is secured, the reaction time will not increase markedly even in a large-

scale carbonation process.

Fig. 19 shows the increase of slag weight caused by the carbonation reaction when the amount of slag was increased from 2 kg to 5 kg and carbonated with the gas flow rate kept unchanged. In this figure, absolute values of weight change are used because the use of carbonation rates, which are all close to 100%, would make it difficult to see the significant differences that exist. By increasing the amount of slag to 10 kg, it became possible at last to confirm the gas utilization efficiency that corresponds to the f-CaO equivalent in the slag. As a result, it was found that slag whose initial f-CaO content is from 4% to 5% could be carbonated with a specific gas consumption of about 20 Nm^3/t -slag.

Fig. 20 shows the results of measuring the changes in the pH of seawater caused by alkaline elution from slag before and after the



Fig. 18 Behavior of temperature and RH during carbonation (10kg)



Fig. 19 Comparison of weight change under several amount of slag



Fig. 20 Behavior of alkaline elution from slag in upscale test

upscale experiment on carbonation. It was confirmed that alkaline elution can be restrained as long as the pH value is 9.5 or less at which the whitening of seawater can be restrained even when the amount of slag is increased.

4.5 Study of practical application of slag carbonation technology at steelworks

(1) Confirmation of carbonation behavior using exhaust gas in the steelworks

As described in the preceding section, it was found that even when the amount of slag was increased to 10 kg, it could be speedily carbonated at room temperature (actually, more speedily than when the amount of slag is much smaller). From the standpoint that when it comes to applying the slag carbonation technology at steelworks, CO_2 contained in various types of exhaust gas that are produced in the steelworks should be utilized effectively, we carried out a laboratory experiment to measure the influence of CO_2 partial pressure on the carbonation rate. In addition, we brought the experimental apparatus shown in Photo 2 to a Works site and carried out a field experiment to verify using exhaust gas (CO_2 content: about 16%) from the limekiln in the grounds of the steelmaking plant.

The outline of the experimental apparatus is shown in **Fig. 21**, and the change in slag weight during carbonation using the exhaust gas from the kiln is shown in **Fig. 22**. The results of a composition analysis of the slag before and after the carbonation treatment are shown in **Table 2**. In Fig. 22, the results of an additional laboratory experiment carried out after the above field experiment under the same CO₂ partial pressure are also shown. It was confirmed that the slag could be sufficiently carbonated using exhaust gases produced in the steelworks.



Fig. 21 Experimental apparatus using exhaust gas in the works



Fig. 22 Behavior of slag carbonation with exhaust gas in the works

	FeO	CaO	SiO ₂	MnO	MgO	P_2O_5	Cr ₂ O ₃	Al ₂ O ₃	t-S	f-CaO
Before test	19.00	41.10	17.00	2.63	2.20	2.47	0.13	2.26	0.256	3.23
After test	17.12	41.50	16.40	2.68	2.19	2.30	0.14	2.22	0.265	1.88

Table 2 Analytical results of slag before and after carbonation using exhaust gas in works (%)

It should be noted, however, that the exhaust gas temperature was somewhat high (40 $\,$) and the slag was easily wetted with dew condensate. For these and other reasons, the carbonation reaction tended to slow down halfway. As shown in Table 2, the f-CaO content of the slag could not be reduced below the target of 1%. We recognize that there is still room for improvement in our slag carbonation technology before it can be put to practical use.

(2) Experiment carried out to find seeds for further improvement in the carbonation rate

In the laboratory experiments on slag carbonation that have been described so far, we employed a stationary process in which the gas is supplied from the bottom of the experimental apparatus as in the case of post-treatment in the existing steam aging equipment. On the other hand, from the results of the upscale experiment shown in Fig. 17, it has been found that as long as the conditions are secured under which wet slag and carbon dioxide (exhaust gas containing carbonation gas) can efficiently make contact with each other, the apparent carbonation reaction at their interface is completed in about 15 minutes. In other words, on the basis of the kinetics theory that it should be possible to promote the overall carbonation reaction by mechanically agitating the slag during the carbonization treatment and thereby actively renewing the slag-gas interface,16) we carried out an additional laboratory experiment in which wet slag was put in a small mixer and carbon dioxide was fed into the upper space inside the mixer. The change in f-CaO content (chemical analysis value) of the slag observed in the experiment is shown in Fig. 23.

It was confirmed from Fig. 23 that the f-CaO content of 10 kg of slag can be reduced to 1% or less in about 20 minutes by carbonation treatment with a gas flow rate of 3 l/min (Fig. 18), and that when the gas flow rate is increased to 10 l/min (in this case, the efficiency of gas utilization decreases), the f-CaO content can be reduced to 1% or less in about 15 minutes, a time that corresponds to the apparent carbonation time in the local reaction zone shown in Figs. 18 and 19. (3) Carbonation test using actual steelworks equipment

On the basis of the results in the series of laboratory experiments described above, we carried out a full-scale test on carbonation of several tons of slag at the steelworks using exhaust gas from the



Fig. 23 Behavior of slag carbonation using stirrer

limekiln (simulated exhaust gas was also used where appropriate) and an existing concrete mixer car or a rotary mixer like a kiln for drying sea-sand (idle equipment) modified into the test equipment. An example of the test equipment is shown in **Photo 7**.

Fig. 24 shows the changes in f-CaO content of slag during carbonation treatment using a concrete mixer car (for batch processing) and a continuous mixer. It has been confirmed that in each of the processes, the f-CaO content of the slag can be reduced to 1% or less in two to four hours (at this level, seawater does not turn white even when the slag is dumped into it).

Samples of the slag that has been carbonated to restrain the elution of alkalis from it are offered to various public organizations, including universities, for exploratory studies for utilization of the sea area in the future. They are also used to assess the influence of the iron contained in slag on the growth of algae,¹⁷⁾ and in exploratory experiments for effective utilization of slag along the coast at various parts of the country.¹⁸⁾ Thus, they help resolve the long-standing problem of seawater whitening by alkaline elution from slag. On the other hand, positive efforts are being made to add new value to steelmaking slag.



Photo 7 Example of full-scale carbonation equipment in the works



Fig. 24 Behavior of f-CaO during full-scale carbonation test in the works

5. Conclusion

Concerning the elution of highly alkaline water from steelmaking slag due to f-CaO contained within-one of the obstacles to expanding the use of slag produced as a by-product of the steelmaking process-we have described the results of our R&D activities to build a slag carbonation process that can be put to practical use. From the standpoint of environmental protection, the demand for effective control of steelmaking slag has become increasingly stringent in recent years. Amid the growing demand for permanent slag control measures and for development of new markets for slag, much is expected of our slag carbonation technology, which allows for effective utilization of CO₂ contained in various types of exhaust gas produced at steelworks (controlling CO, emissions is also strongly called for from the standpoint of curbing global warming), and that permits economically resolving the long-standing problems inherent to the handling of steelmaking slag. In the future, we intend to continue making strenuous efforts to further improve our slag carbonation technology in close cooperation with all the departments concerned as part of the environmental activities of Nippon Steel.

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