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PROPOSITION OF COMPOSITE DETERIORATION COUNTERMEASURE METHOD FOR CHLORIDE ATTACK AND CARBONATION USING LITHIUM NITRITE MIXED GEL

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ABSTRACT:

The highway in the Hokuriku region may have an early progress of chloride attack as anti-freezing agent is sprayed in winter. Also it is easy to progress carbonation at RC floor in the steel bridge slab or RC hollow floor slab because of low W/C and thin cover thickness, as compared to other structural types. As a result, there is concern about complex deterioration due to chloride attack and carbonation of reinforced concrete. Herein when deteriorations rate is high under not single factor but combined factors. As a countermeasure there is a method of thinly applying a repair mortar mixed with a high concentration nitrite-based rust preventive agent to existing concrete, and an effect of suppressing composite deterioration of these is reported. However, when applying to the ceiling surface such as the lower part of the floor slab by the plastering method, workability declines. In this study, lithium nitrite was used. Nitrite ion rehabilitates the passive film of the reinforcing bar and aims at suppressing the carbonation by the water holding property of the gel. First, basic experiments were carried out using specimens prepared in the laboratory, and the effect of inhibiting nitrite ion penetration and carbonation was compared with the conventional method and clarified. Next, evaluation tests that can be used in actual slabs were also carried out by using the collected core of the deck removed by chloride attack and carbonation. As a result, we clarified that nitrite ion has internal penetration early and has neutralization inhibiting effect at the early stage.

KEYWORDS: Composite deterioration,Chloride attack, Carbonation, Gel composed lithium nitrite, Nitrite ion

1. Introduction

A large amount of flying salt is carried by winter seasonal wind to the structure in the Hokuriku region. This is confirmed mainly at bridges located near the coast. Also anti-freezing agents are sprayed at road bridges as a countermeasure against slipping accidents caused by freezing in winter. When these chlorides penetrate in RC, the rebar rusts. Then, the volume increases, and cracks and peeling occur in concrete, thereby deterioration is promoted.

In addition, the progress of carbonation tends to be faster as compared with other structural types, such as steel bridge RC floor slabs and RC hollow floor decks [1]. As a result, the decrease of pH in concrete may destroy the passive film of the rebar and cause corrosion.

In the Hokuriku region, since these phenomena occur simultaneously, complex deterioration is concerned. In this case, the hydrate that fixed the chloride ion is broken by carbonation and becomes soluble, and the chloride ion concentrates and moves to the inside, so it proceeds faster than single degradation [2].

In general, nitrous acid corrosion inhibitor is used as a rust inhibitor to prevent corrosion of rebar. This is aimed prevention of rebar corrosion by re-forming a passive film to using nitrite ion as an oxidizing agent. In the United States, construction methods for protection of rebar corrosion are studied by mixing this nitrous acid corrosion inhibitor in fresh concrete [3]. However, there are few research painting on existing concrete structures. In the past, a method of mixing high nitrous acid corrosion inhibitor in Polymer modified mortar and thinly coating it on the surface of existing concrete by 2 mm thickness has been studied in Japan. It has been reported that it can suppress the chloride corrosion of rebar [4] [5] and the compound deterioration with carbonation [2]. In this method, the upward application to the deck is applied by the plastering method. However, due to difficulty in construction, there are problems such as poor workability.

Therefore, a new method incorporating Lithium Nitrite directly into the gel is developed. Since the gel has adhesive strength, it can be applied to the side and bottom of the deck. In addition, since Lithium Nitrite can be directly incorporated into the gel, it is expected that a larger amount of Lithium Nitrite can be mixed in compared with Polymer modified mortar.

Based on the above background, a gel containing Lithium Nitrite is developed. In addition, the amount of penetration of nitrite ion as a rust preventive component is evaluated. Furthermore, the effect of suppressing carbonation is also evaluated.

The flow of this study is as follows. First, in basic experiments, a new application method using a gel is proposed, and the permeability of the rust preventive component is confirmed. The carbonation inhibiting effect is also clarified. Next, in applied experiments, confirmation of whether the nitrite ion penetration effect and carbonation inhibition effect obtained in the basic experiment can be expected in the actual slab is verified using the removed floor slab.

2. Basic experiment

2.1 Experiment case

Experiment case is shown in Table 1. Also the configuration of specimen is shown in Figure 1. Ordinaly portland cement is used. Mortar (W/C=60%) is prepared and coated with epoxy resin except the one surface. Next, in order to simulate the carbonated existing slab, the carbonation accelerated exposure (40 ℃, RH=60%, CO_2=5.0%) is performed for 10 weeks and carbonated depth about 10mm. Thereafter, a gel mixed with Lithium nitrite is applied to the mortar surface. Here, the gel is a Lithium Nitrite (45%) aqueous solution with a modified acrylamide type thickener. Also, Lithium Nitrite and the thickener are mixed at a mass ratio of 100: 6, and the viscosity is adjusted to be about 30,000 mPa· s. This corresponds to the viscosity that can be applied to the concrete surface with a roller. A photograph of the case coated with gel is shown in Figure 2.

Table 1 Experiment case

Case	Coated amount (g/m^2)	Lithium Nitrite amount (g/m^2)	Coating medium	Coating method	Coating thickness (mm)
Blank	-	-	-	-	-
A	500	225	Gel	Roller	0.5
B	1000	450		Rubber bellows	1.0

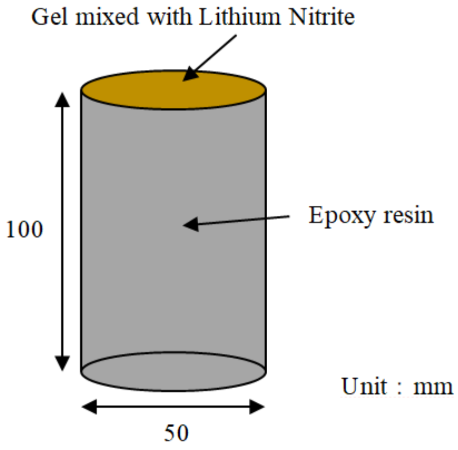

Figure 1 Specimen configuration.

Figure 2 Photograph of case coated with gel.
(Immediately after coating)

2.2 Test method

The test items are (1) the amount of penetration of nitrite ion and (2) the carbonation depth. Here, (1) specimens for measuring the amount of penetration of nitrite ion is exposed in Kanazawa City from the end of October for 3 months and 6 months. Also, a roof is set up so as not to be affected by rain or snow. After exposure, the gel is removed and the specimen is sliced every 5 mm. Subsequently, the permeability of nitrite ion is measured by ion chromatography according to “JIS A 1154 method of test for chloride ion contained in hardened concrete (analysis method of warm water extracted chloride ions contained in Annex B hardened concrete)”. Next, the accelerated carbonation exposure is carried out for 3 months and 12 months accordance with “JIS A 1153 method of accelerated carbonation test for concrete”. After that, splitting the specimen and the carbonation depth is measured in accordance with “JIS A 1152 method of measuring carbonation depth of concrete”.

2.3 Test results

2.3.1 Amount of nitrite ion

Figure 3 and Figure 4 show the amount of penetration of nitrite ion at the 3 months and 6 months of outdoor exposure. According to these, it is recognized that the values of nitrite ion permeates higher in case B as compared with case A. Also, in both cases, the maximum values of nitrite ion amount at the 3 months and 6 months are at the depth of between 10 and 20 mm. Herein, pre-carbonated depth of the specimens is between 0 and 10 mm. Also it has been confirmed that chloride ion goes through a carbonation region smoothly when both carbonation and chloride attack are progress. Therefore this phenomenon seems to be that the nitrite ion is concentrated to the deep part by the same mechanism [6].

Figure 5 shows the total amount (integrated value) of nitrite ions after the general rebar positions (depth: 20 mm) such as RC deck slab in Japan. In addition, it is compared with the case where Lithium nitrite is mixed in Polymer modified mortar which is a conventional research method. In the case of Polymer modified mortar, the result of mixing 100 kg/m^3 of Lithium nitrite in the study conducted by Fujita et al. is compared as case C [7]. According to this, it is recognized that case B in which the amount of Lithium Nitrite is the largest permeates about 70 times more than in case C in 3 months and 6 months. This reason can be thought that Lithium Nitrite penetrated into the mortar at an early stage because of the water solubility of the gel, but Lithium Nitrite stays in the Polymer modified mortar when it is mixed in the Polymer modified mortar.

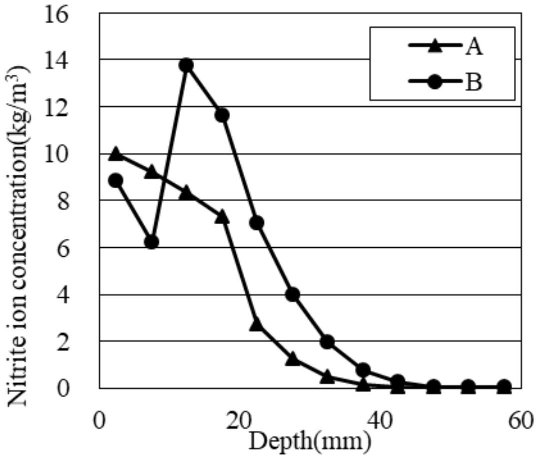

Figure 3 Nitrite ion concentration (3 months).

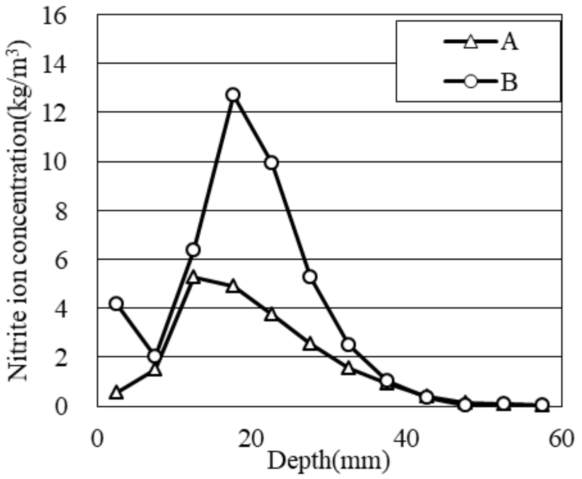

Figure 4 Nitrite ion concentration (6 months).

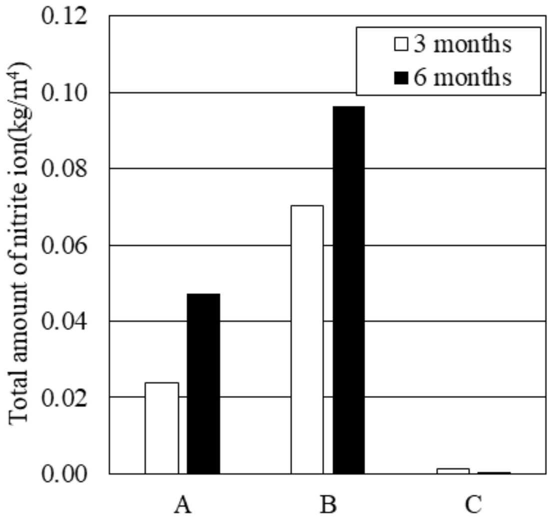

Figure 5 Total amount of nitrite ion (integral value).

2.3.2 Carbonation depth

Figure 6 shows the carbonation depth at accelerated carbonation exposure 3 months and 12 months. According to this, it is recognized that the carbonation depth is suppressed to about 70% in case B as compared with Blank. On the other hand, carbonation inhibiting effect is observed but quite low in case A. It is considered that the drying of the gel accelerated as the circulating wind is flowing through the chamber during the accelerated carbonation exposure. As a result, this reason can be thought that Lithium Nitrite don't sufficiently penetrate because the environment become easy to evaporate moisture from the gel.

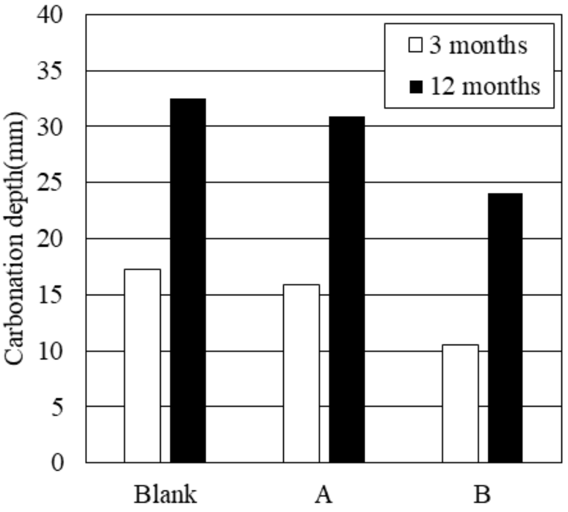

Figure 6 Carbonation depth.

3. Application experiment

3.1 Experiment case

In section 2, it is recognized that the amount of penetration of nitrite ion is large and penetrates deeply when gel is applied as compared with the conventional method using Polymer modified mortar. In this section, applications of new gel method to existing concrete and new concrete are simulated. As a result, demonstrated is the amount of penetration of nitrite ion and the carbonation inhibiting effect by using the core which was removed from an actual deck. In addition, the presence or absence of carbonated part is simulated to compare the effects when this methods apply to existing concrete and new concrete.

Table 2 shows the experimental cases. As shown in Figure 7, the specimens are the cores taken from the lower surface of the steel bridge RC slabs (W/C=51%, C=300kg/m^3) that has been placed for more than 40 years after construction and replaced due to chloride attack and carbonation. The height of core is about 150 mm. After that, it is divided into places of about 75 mm in height. The specimen containing the surface part of the slab is regarded as the carbonated part, while the specimen not including the surface part of the slab is regarded as the un-carbonated part. After cutting specimen into a semicircle, it is coated with an epoxy resin without a test surface, and the same amount of gel as described in section 2 is applied upward using a trowel. A photograph of the specimen is shown in Figure 8. The coating amount is set to 1,000g/m^2 which can confirm the effect of suppressing carbonation in section 2.

Table 2 Experiment case

Case	Already carbonation	Coating amount (g/m²)	Lithium Nitrite amount(g/m²)	Coating medium	Coating method
Cblank	Carbonated	-	-	-	-
C1000		1000	450	Gel	Trowel
UCblank	Un-carbonated	-	-	-	-
UC1000		1000	450	Gel	Trowel

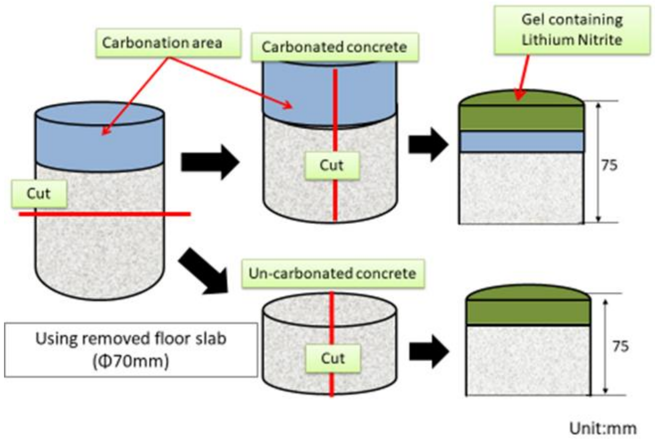

Figure 7 Specimen configuration.

Figure 8 Specimen coating with gel.

3.2 Test method

As same in 2.2, the test items are (1) the permeability of nitrite ion, (2) the carbonation depth. Here, (1) the permeability of nitrite ion is measured after outdoor exposure from 4 weeks to 48 weeks.

3.3 Test results

3.3.1 Amount of nitrite ion

Table 3 shows the carbonation depth at the time of cutting out. Also, Figure 9 and Figure 10 show the nitrite ion permeation distribution at each week. According to Figure 10, it is recognized that the nitrite ion concentration is higher in the surface layer part and lower in the inner part in the case of un-carbonated concrete. On the other hand, in the case with carbonated concrete shown in Figure 9, it is recognized that as the exposure period is extended, the value becomes constant in the range from the surface layer to about 30 mm. In addition, it is recognized that the maximum value of nitrite ion concentration is deepened about 20 mm in the case with carbonated concrete compared to the case with un-carbonated concrete. As shown in Table 4, the area of between about 0 and 30 mm is carbonated in the specimen beforehand. Therefore, as shown in Figure 11, this reason will be considered moisture containing nitrite ion which is present in the surface layer part quickly penetrate into the carbonation zone immediately after coating and cause migration and concentration phenomenon to the un-carbonated zone.

Table 3 Carbonation depth of specimen evaluated permeability of nitrite ion

Exposure(week)	Carbonation depth at cutting out(mm)
1	30.6
4	31.0
12	28.5
36	24.4
48	34.4

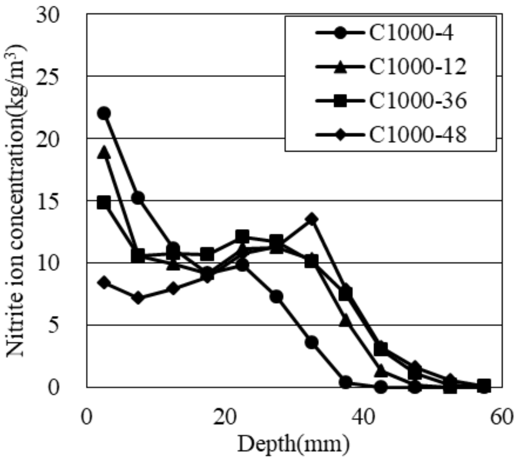

Figure 9 Nitrite ion concentration (Carbonated).

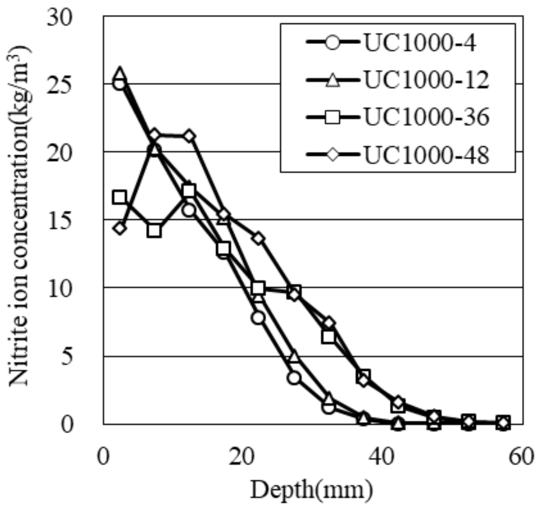

Figure 10 Nitrite ion concentration (Un-carbonated).

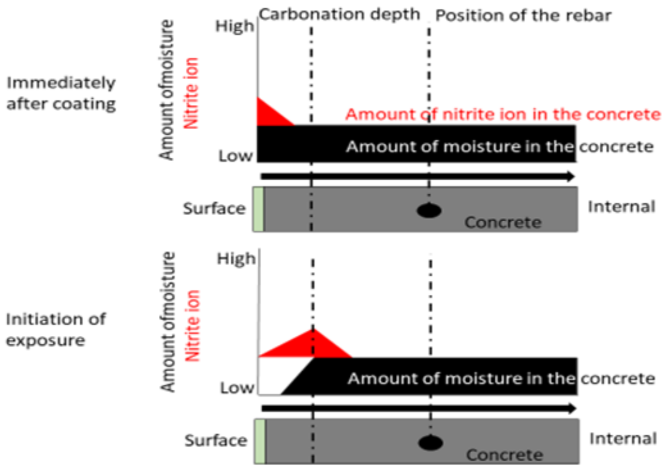

Figure 11 Mechanism of movement and concentration phenomena.

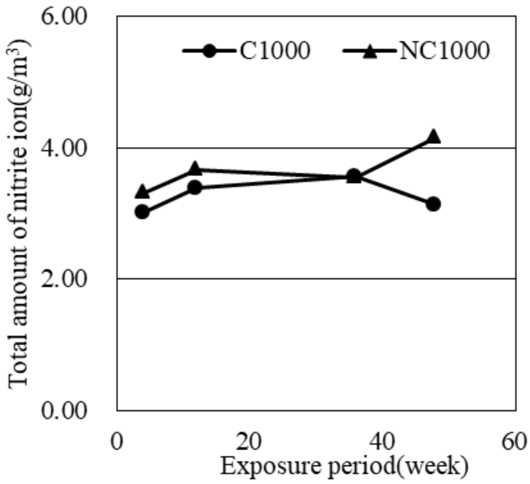

Figure 12 Total amount of nitrite ion (All).

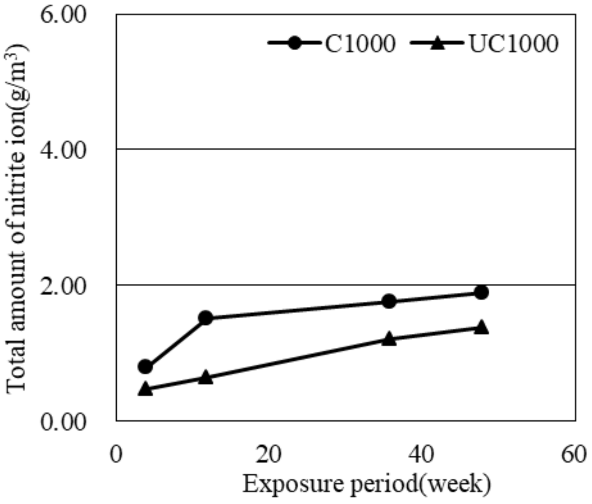

Figure 13 Total amount of nitrite ion (20～60mm).

3.3.2 Carbonation depth

Table 4 and Figure 14 show the carbonation depth at the time of core extraction and after exposure for 48 weeks. In addition, [C] is the value that has progressed during the 48 weeks accelerated exposure period the carbonation depth [A] at the time of core extraction which minus from the carbonation depth [B] after the accelerated carbonation exposure. Next, in order to evaluate the effect of application, the carbonation depth in the case of application and without application is compared. According to these results, it is recognized that [C] when gel is applied becomes about 40%, compared to [C] without application, in the case of carbonation. Moreover, it is recognized that [C] when gel is applied becomes about 60%, compared to [C] without application, in the case without carbonation. This reason can be thought that carbonation is suppressed because Lithium Nitrite contained in the gel become Lithium Hydroxide, thereby suppressing pH decrease [8]. Also, it is recognized that the effect of suppressing carbonation is equivalent regardless of the presence or absence of carbonation.

Table 4 Carbonation depth

Case	Exposure term (Week)	Carbonation depth(mm)		
		The time at cutting [A]	The time after the exposure [B]	Progress during exposure [B]-[A]=[C]
CBlank	48	28.1	60.9	32.8
UCBlank		0.0	66.3	66.3
C1000		35.0	56.6	21.6
UC1000		0.0	29.7	29.7

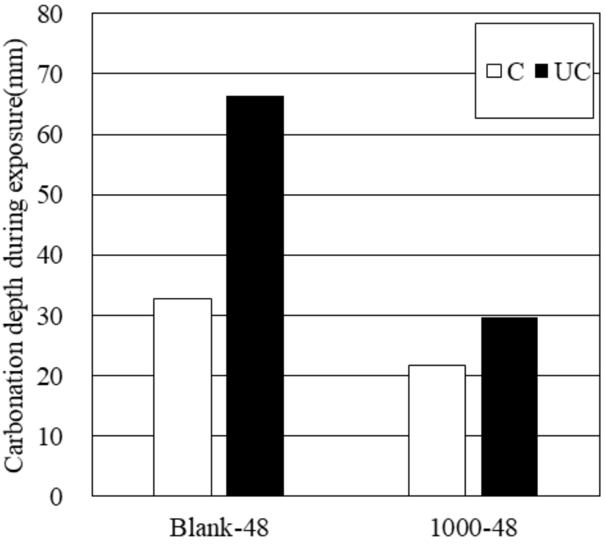

Figure 14 Carbonation depth advanced

4. Conclusion

1) Preventive maintenance method against combined deterioration of chloride attack and carbonation is developed. A gel obtained by thickening a 45% Lithium Nitrite aqueous solution with a modified acrylamide thickener is used. The feature of this method is that it can be easily applied upward.

2) Nitrite ion is a rust preventive component and permeated into concrete similarly to case in reference [7] when Lithium Nitrite is mixed in Polymer modified mortar. In particular, it does not stay in the already carbonated zone and penetrated deeper.

3) When the coating amount is 500g/m^2, the effect of suppressing carbonation is recognized but quite low. On the other hand, when the coating amount is 1000g/m^2, the effect of suppressing carbonation is recognized. For example, in applied experiments, carbonation depth [C] advanced by accelerated exposure can be confirmed to decrease by 11.2 mm compared to non-application when there is carbonation

4) The amount of nitrite ion permeation due to the presence or absence of carbonation is almost equal in comparison with the total amount. On the other hand, when comparing after the position of the rebar, the case with carbonation penetrated about 40% more than the case without carbonation.

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