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RELATION BETWEEN CORROSION OF THE REINFORCEMENT AND CARBONIZATION IN THE CONCRETE CONTAINING CHLORIDE

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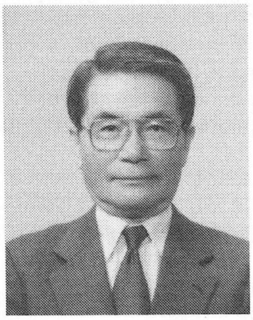

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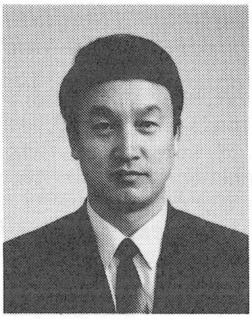
Kazusuke kobayashi



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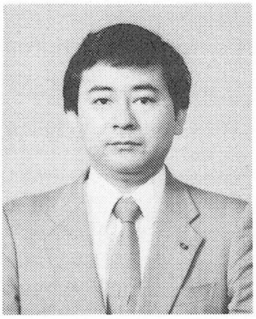

Yuichi Uno

SYNOPSIS

This paper deals with the influence of carbonation depth of concrete on reinforcing bar corrosion occurring in concrete containing chloride such as those found in sea sand. First, while investigating the relationship between reinforcing bar corrosion and the carbonation depth of concrete into which chloride were mixed in, the area analysis by EPMA was conducted for chlorine and sulphur for a concrete cross section. Based on the findings, this paper elucidates that reinforcing bar corrosion is initiated before carbonation front reaches the surface of the reinforcing bars, because, when carbonation of concrete containing chlorides advances, it causes enrichment of chlorides to move toward the non-carbonated zone.

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1.INTRODUCTION

Kishitani and Kashino [1], who are among the authors made an investigation on the relation between the depth of carbonation of concrete and corrosion of the reinforcement and clarified that corrosion is not initiated after the front of carbonation has reached the surface of the reinforcement,but begins at fairly earlier stage than that. In other words,they defined the difference between the thickness of cover of the reinforcing bar and the critical depth of carbonation at which corrosion begin as "residual depth for carbonation" and stated that the residual depth for carbonation is about 20 mm for concrete that contains chlorides and 8 mm for concrete with no chlorides. In the meantime, Kobayashi and Uno [2] made clear that as carbonation proceeds in the concrete structure that contains chlorides, chlorine that has existed in the carbonated zone moves toward the interior of structure, raising the concentration of chlorine in the uncarbonated zone consequently. In this paper, a novel view on the mechanism of corrosion of the reinforcement due to carbonation of concrete structure that contains chlorides is presented which is gained by combining the relation between corrosion and carbonation of the reinforcement that was discovered by kishitani and Kashino and the concentrating phenomenon of chlorine induced by the carbonation of the concrete that was made clear by Kobayashi and Uno.

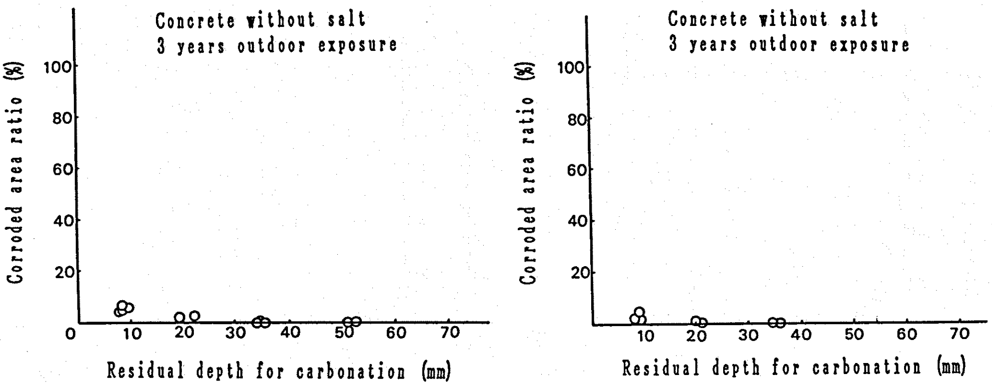
2.RELATION BETWEEN THE INITIATION OF CORROSION OF THE REINFORCEMENT AND THE PROGRESS OF CARBONATION

2.1 Outline

Cylindrical concrete specimens with a steel bar embedded at the center of each specimens are provided. They are exposed in the outdoor environment and the accelerated carbonation for the specified length of time as carbonation proceeds. After that, the relation between the depth of carbonation and corrosion of the reinforcement is investigated. Specimens made of concrete of two types of mix proportion, namely, the one added with chlorides and the other without any chloride are tested.

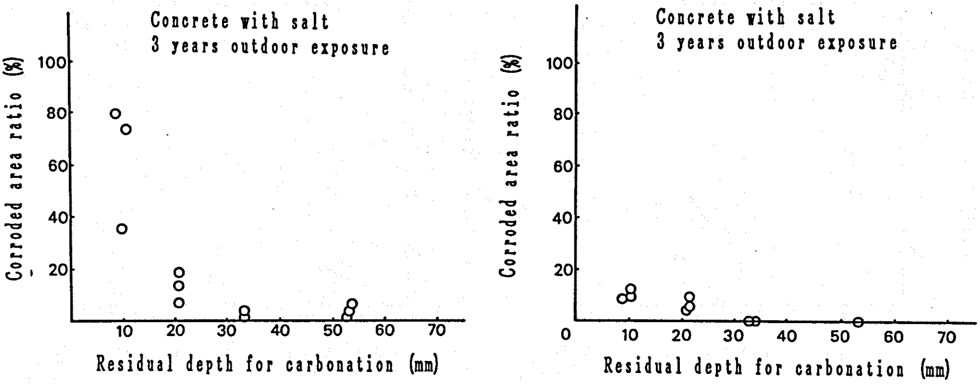
2.2 Method of Testing

The materials used are ordinary Portland cement,coarse aggregate whose maximum size is 10 mm,river sand and distilled water. Regarding the mix proportion,the water content is determined so as to gain 11 cm slump at the water cement ratio of 70 %, and two types of specimens are provided and tested,namely,the one added with 2.87 kg/m3 NaCl by means of artificially made sea water and the other that contains no NaCl. With regard to the size of specimens,four types which are ø 5 x 10 cm, ø 7.5 x 15 cm, ø 10 cm x 20 cm and ø 15 cm x 30 cm are tested. Every specimen has a finished steel bar of 16 mm embedded at its center. By arranging the steel bar as mentioned above, the thickness of cover is made to be approxiappmately 20,30,40 and 70 mm respectively. After concrete has been placed,the specimens are cured in the chamber at 20°C and 80 % RH for one week. Thereafter,they are subjected to carbonation in the environments of two kinds, namely,in the outdoor environment and an atmosphere of carbon dioxide (CO_2 concentration 5 % and 30°C). With respected to the specimens exposed to the outdoor environment, measurement of the depth of carbonation with phenolphthalein and that of the corroded area ratio of the steel bar are conducted after 1, 2 and 3 years are elapsed. And as for the specimens subjected to accelerated carbonation in the carbon dioxide, they are taken out of the accelerated carbonation chamber when their carbonation depth has reached 30 mm and 50 mm respectively and are preserved indoors for 2 years after which the similar tests are done.



(a) corrosion of G type (b) corrosion of D type

Fig.1 Corroded area ratio and residual depth for carbonation

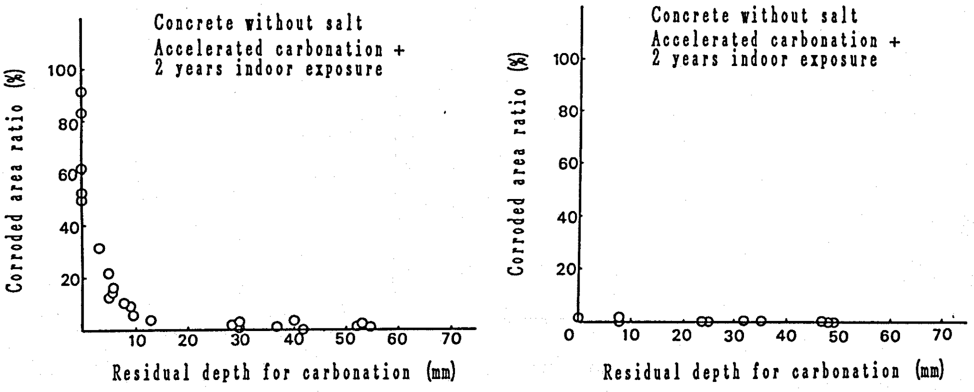


(a) corrosion of G type (b) corrosion of D type

Fig.2 Corroded area ratio and residual depth for carbonation

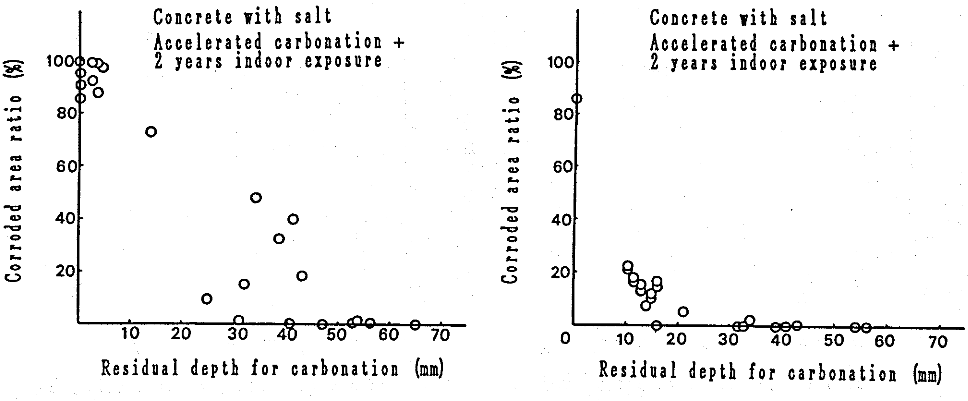
2.3 Results and Discussion

In Fig. 1 and Fig. 2, the relations of the "residual depth for carbonation" and the corroded area ratio of the steel bar in the specimens that have been exposed to the outdoor environment for 3 years are shown for the specimens to which sodium chloride was added and those without its addition respectively. The corroded area ratios of the reinforcing bars are indicated classified into the general corrosion (corrosion of G type) which means the type of corrosion that grows uniformly and quickly and the pitting corrosion (corrosion of D type) in each figures. As clearly seen in these figures, corrosion of the reinforcing bar does not begin at the time when the front of carbonation has reached its surface as judged by the color reaction in which the phenolphthalein solution is used, but does not start when it reaches a point on the way to the surface of the reinforcing bar that leaves a certain distance (residual depth for carbonation) to it. Table 1 shows the value of the residual depth for carbonation estimated from the summary of the results obtained from these figures and investigations made on numerous concrete structures. According to this table, in concrete that



(a) corrosion of G type (b) corrosion of D type

Fig.3 Corroded area ratio and residual depth for carbonation



(a) corrosion of G type (b) corrosion of D type

Fig.4 Corroded area ratio and residual depth for carbonation

does not contain chloride, corrosion of the type D is occurred at the time when the "residual depth for carbonation " reached 8 mm and in concrete with chloride it begins at the 20 mm of the "residual depth for carbonation". The fact means that the reinforcing bar at the position where concrete presents distinct red color by the color reaction of phenolphthalein solution already begins to corrode. Furthermore, Table 1 tells that existence of chloride within concrete greatly affects the "residual depth for carbonation" and the "residual depth for carbonation" of concrete that contains chloride is greater than that of concrete without chloride by as much as 10 mm and above. In addition to the above, Fig 3, Fig.4 and Table 2 show the result of tests in the cases of accelerated carbonation. As made clear by Table 1 and Table 2, the relation between the "residual depth for carbonation" and corrosion of the reinforcing bar in case of the specimen that was exposed in the outdoor environment differs little from the same in case of the specimens that underwent accelerated carbonation. Fig 5 and Fig 6 show the relations between the "residual depth for carbonation" and corrosion of the reinforcing bar summarizing both cases of exposure in the outdoor environment and accelerated carbonation.

Table.1 Residual depth for carbonation of concrete after 3 years outdoor exposure

kind of concrete \ type of corrosion	G-type	D-type
With salt	10 mm	8 mm
Without salt ※	30 mm	20 mm

※ NaCl = 0.3%/sand

Table.2 Residual depth for carbonation of concrete subjected to accelerated carbonation

kind of concrete \ type of corrosion	G-type	D-type
With salt	10 mm	8 mm
Without salt ※	43 mm	21 mm

※ NaCl = 0.3%/sand

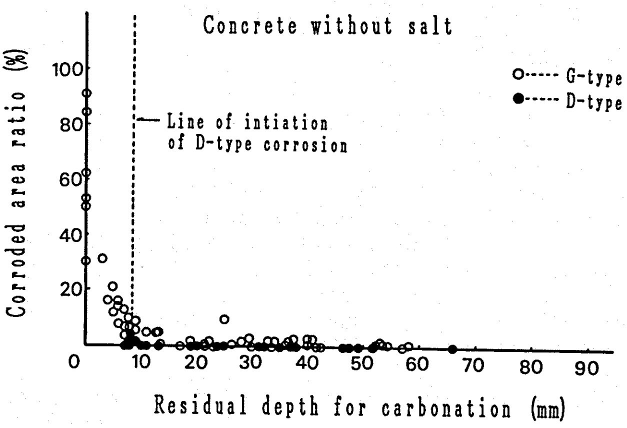


Fig.5 Corroded area ratio and residual depth for carbonation

3.CONDENSATION OF CHLORINE AND SULPHUR DUE TO CARBONATION OF CONCRETE

3.1 Outline

Specimens of mortar to which chloride is added are provided and accelerated carbonation process is applied to them. The distribution of chlorine concentration at the cross section of the specimen is investigated through the

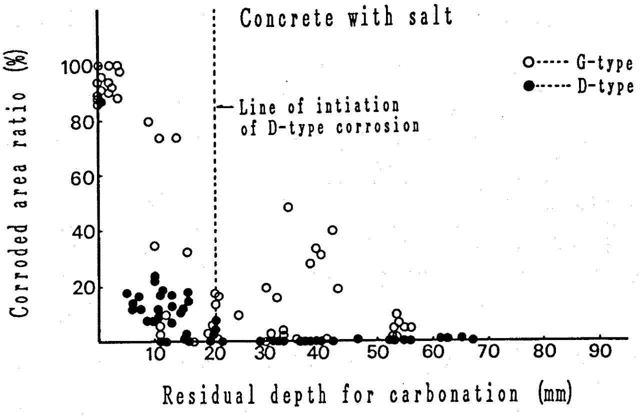


Fig.6 Corroded area ratio and residual depth for carbonation

area analysis by EPMA, thereafter. As its result, it is made clear that in mortar that contains chlorides, chlorine moves toward the interior of the specimen as carbonation of mortar makes progress, thus causing its condensation. In addition to this, the cores are taken from the concrete pier of highway bridge and the concrete foundation of the building that elapsed more than 10 years after their construction and the distribution of chlorine or sulphur in there cross section by the similar method to the above. As the result, it is verified that the similar phenomena to those that were found in the laboratory test takes place in the actual concrete structures.

3.2 Method of Experiment

Mortar was prepared by mixing ordinary Portland cement of R_2O = 0.57% (C),silica sand (S) and ion-exchanged water (W). Its mix proportion was W:C:S = 0.5: 1:2.25. The additives used for adding chloride was $CaCl_2$. In other words,under the assumption that all $CaCl_2$ was dissolved into ions,$CaCl_2$ is added by dissolving into the mixing water so that the quantity of the chloride ions in concrete reaches 2.4 kg/m3. Besides, NaOH was added so that the equivalent quantity of Na_2O of cement becomes 1.5% for the purpose of accelerating carbonation. The specimens were cylinders of Ø 5 x 10 cm,.with fog curing done at 20°C for 28 days after casting. Immediately after curing has been finished, accelerated carbonation is applied in the environment of CO_2 concentration 10%,20°C and 60% RH. At each time when 2, 8 and 16 weeks of accelerated carbonation have elapsed,the area analysis by EPMA was conducted. By the way, in the case of 16 weeks,the quantitative analysis is conducted by the wet method to measure the quantity of chlorine. The area analysis by EPMA was carried out on the test piece of a disc shape of Ø 5 mm thick that is cut out at the middle of the specimen after applying preparatory processes such as fine grinding, carbon vaporization etc.

3.3 Results and Discussion

Fig.7-9 present the conditions of chlorine distribution obtained from the area analysis by EPMA. They show the result of analysis just before starting accelerated carbonation, at the times when 2 weeks of accelerated carbonation and 16 weeks of the same have finished respectively. In these figures, the bright part shows the area where intensity of X-ray is high and concentration of

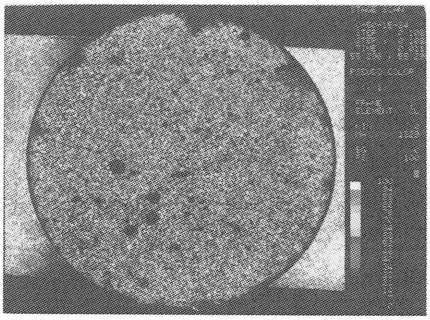


Fig.7 X-ray image map of Cl on the polished surface of mortar

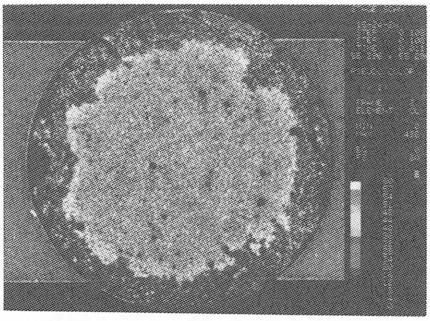


Fig.8 X-ray image map of Cl on the polished surface of mortar

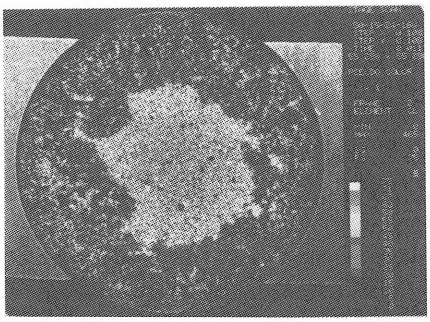


Fig.9 X-ray image map of Cl on the polished surface of mortar

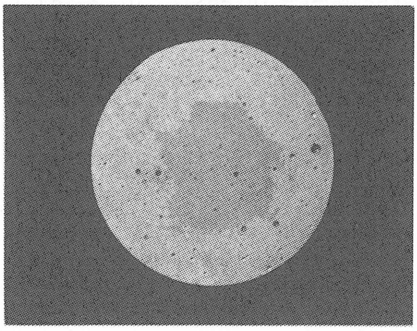


Fig.10 Carbonation profile of mortar

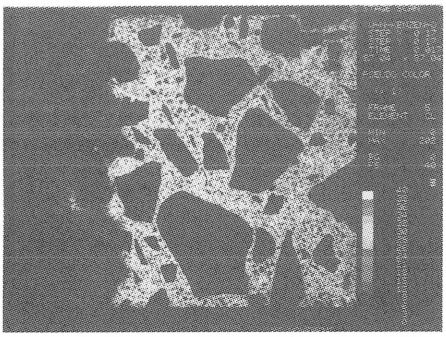


Fig.11 X-ray image map of Cl on the polished surface of concrete core

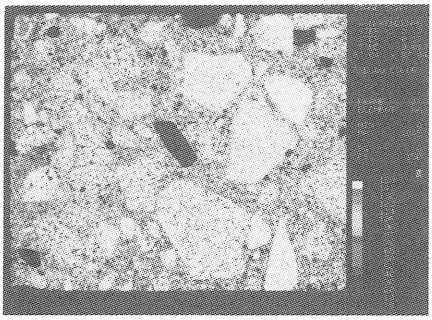


Fig.12 X-ray image map of S on the polished surface of concrete core

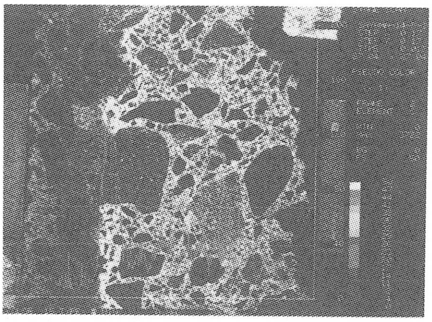


Fig.13 X-ray image map of S on the polished surface of concrete core

chlorine is high and the dark part shows the area where intensity of X-ray is low and concentration of chlorine is low. From these figures, it is known that the conditions of chlorine distribution of the specimen subjected to accelerated carbonation for 2 weeks or longer present two clearly divided areas, namely the area close to the surface of the specimen where the concentration is low and the area around the center line where the concentration is higher. On the other hand, when Fig.10 which shows the carbonated portion of the specimen carbonated for 16 weeks by the phenolphthalein color reaction is compared with Fig.9, the boundary of the areas that different concentration as seen in this Figure almost coincides with the boundary between the carbonated area and the non-carbonated area. This fact means that chlorine that was distributed almost uniformly in the cross section of the specimen moves as carbonation proceeds from the carbonated area to the uncarbonated area and as its consequence, the chlorine concentration in the carbonated area has become very low and inversely condensation of chlorine has taken place in the uncarbonated area. The reason why movement and condensation of chlorine take place in mortar that contain chlorine as carbonation proceeds is as the followings [3].:

1) Out of the chloride ions in chlorides that are contained in mortar, up to about 0.4% of the weight of cement are fixed as Friedel's salt.

2) Due to carbonation, this Friedel's salt is decomposed into $CaCO_3$, $Al(OH)_3$ and $CaCl_2$.

3) Since $CaCl_2$ is water-soluble, chlorine once fixed as Friedel's salt ionizes into the pore solution.

4) Chloride ions thus generated move out to the uncarbonated area by concentration diffusion from the carbonated area and are fixed again as Friedel's salt which causes condensation.

In order to verify whether the above mentioned phenomenon that was clear in the laboratory tests would have been taken place in actual structures, cores are taken from the concrete piers of highway bridge that elapsed more than 20 years after completion and the distribution of chlorine and sulphur within them from the surface toward the center is investigated by EPMA in the similar way to the case of the laboratory test. In these cores, a lot of shells are included which evidences that marine sand was used as aggregate almost without being desalted. Fig. 11 shows the condensations of chlorine distribution from which it is known that little chlorine exists at about the depth of 2.5 cm and chlorine concentration rises toward interior. In this case, too, the area over which little chlorine exists and the carbonated area that is determined by the phnolphthalein solution exactly coincide. Furthermore, what is worthy of attention is that just the same phenomenon as observed in the laboratory test that the chlorine concentration just inside of the front of carbonation conspicuously rises takes place. The result of analysis as mentioned above shows that the movement of chlorine toward inside and condensation of chlorine take place in the actual structures,too,as carbonation proceeds. Fig.12 shows the conditions of sulphur distribution on the surface of the same specimen. From this figure, in this case of sulphur also, quite similarly to the case of chlorine, it is known that its concentration is very low in the carbonated area and condensation of sulphur takes place inside. And Fig.13 presents the result of investigation by EPMA made on the condition of sulphur distribution from the surface of the interior of the core taken from the concrete foundation of the building 10 years after completion in the suburbs of Tokyo. In this case, too, the same result as seen in Fig.11 is gained. Aforementioned results all indicate that regardless of existence or non-existence of chlorine within concrete, sulphur also moves toward inside from the surface as carbonation proceeds and is condensed there.

4. CORROSION AND CARBONATION OF REINFORCING BARS IN CONCRETE THAT CONTAINS CHLORIDES

Based upon the phenomena that were made clear in Section 3, the distribution of concentration of chloride ions and sulphate ions in the cross section of the reinforced concrete member that contains chlorides is schematically presented in Fig. 14. From this figure,it is known that as carbonation proceeds in the concrete structures that contain chlorides, there always exists a zone just inside of the carbonation front where concentration of sulphur is remarkably high and in this zone the concentration of OH^- is reduced as those of Cl^- and SO_4^{--} increase there. Accordingly, if there exists any reinforcing bar in this zone, corrosion of the reinforcement is started before the carbonation front reaches it. The result of experiment reported in Section 2 can be explained with such mechanism of corrosion. And in the concrete structure that contains chloride little, if condensation of sulphuric compound takes place, corrosion of the reinforcement will be generated. For, in common cement, considerable amount of sulphuric compounds exist in the form of alkali sulphate and gypsum. The ground on which the residual depth for carbonation in concrete that contains no

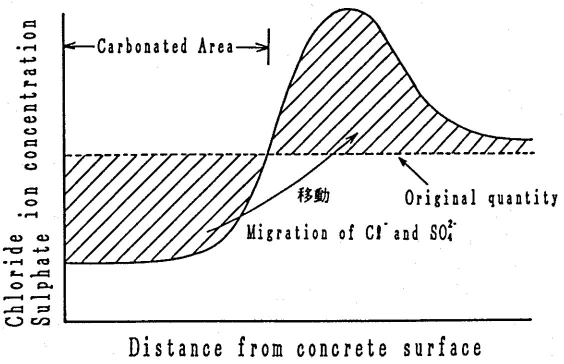


Fig.14 Cl concentration profile in concrte structures

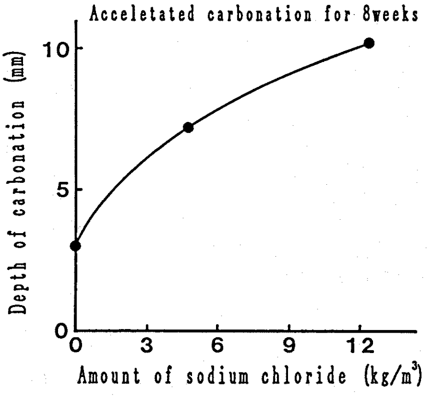


Fig.15 Amount of NaCl in mortar and depth of carbonation [4]

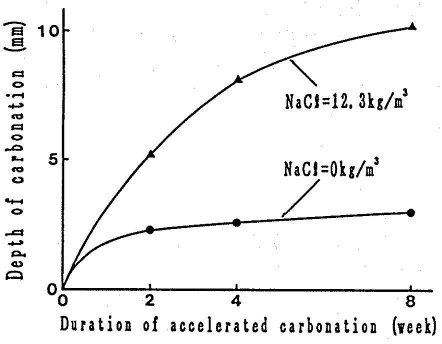


Fig.16 Effect of NaCl content on carbonation depth of mortar [4]

chloride was concluded to be 8 mm in Section 2 may be explained in this way. On the other hand, sodium chloride that is introduced from marine sand expedite carbonation of concrete as shown in Fig. 15. And this accelerating becomes more conspicuous as the content of sodium chloride increase as shown in Fig.16. Based upon the abovementioned results, an investigation is made on how fast the rate of corrosion of the reinforcement will be when the concrete structure that contains chloride is carbonated, by using Kishitani's formula (1) [5] which has been most popularly applied to the estimation of the rate of carbonation and the result obtained is as following;

$$t = 7.2\,X^2 / R^2(4.6W - 1.76)^2 \qquad (W \leq 0.6) \qquad (1)$$

where, t = exposure time(years) W = water cement ratio
X = depth of carbonation (cm)
R = constant concerning kind of cements,aggregates and admixtures.

According to the conventional concept, it takes as long time as 222 years until the carbonation front reaches the reinforcing bars that are arranged at the depth of 30 mm from the surface. However, according to the conclusion obtained so far in this paper, the time upon which corrosion of the reinforcing bar begins is when the front has reached the point 20 mm off the surface or depth of carbonation reached 10 mm and it needs a period of 24 years. Furthermore, if the acceleration effect of the existence of sodium chloride on carbonation is taken into consideration, this period becomes shorter. Since the value of the residual depth for carbonation 20 mm is obtained through the accelerated carbonation tests, it may not be applied to the actual concrete structures as it is. However, if the ratio of the degree of carbonation in the case when chloride ions of 1.4 kg/m3 are included to that in the case when no chloride exists in concrete is taken, its value shows about 2 times which means corrosion of the reinforcing bars will begin in about 12th year.

5. CONCLUSION

The facts made clear with regard to the relation between corrosion of the reinforcing bars in concrete that contains chlorides and the depth of carbonation in this study are summarized as the followings:

1) Corrosion of the reinforcing bars caused by carbonation begins prior to the time when the carbonation front reaches the surface of the reinforcement. If the degree of carbonation at the critical point upon which corrosion begins is defined as the residual depth for carbonation (difference between the thickness of cover and the depth of carbonation) its value becomes about 20 mm for concrete that contains chlorides and about 8 mm for concrete that contains no chlorides.

2) The reason why corrosion of the reinforcement begins at the point prior to the time when the carbonation front reaches the surface of the reinforcing bars is that in the case of concrete that contains chlorides, the chloride ions that were once fixed as Friedel′s salt are dissociated as carbonation proceeds, move out to the non-carbonated zone by concentration diffusion and are condensed, and in the case of concrete that contains no chloride, the sulphate ions that were once fixed as ettringite are dissociated and move out and are condensed similarly to the case of condensation of chloride ions.

3) Since sodium chloride that is contained in marine sand expedites carbonation of concrete as well as causes condensation as mentioned above, thus the time on which corrosion of the reinforcing bar begins is made earlier.

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