

STUDY ON ESTIMATION OF DISTRIBUTION OF CHLORIDE IONS CONTENT ON SURFACE AREA OF CONCRETE MEMBER COMBINING ELECTROMAGNETIC WAVE METHOD AND X-RAY FLUORESCENCE METHOD

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Abstract: In the case of deterioration caused by corrosion expansion of reinforcing bars such as salt damage, large damages cannot be found on the concrete surface until cracking. In order to estimate the progress of salt damage, the authors have been investigating to estimate content of chloride ions using electromagnetic waves, which is one of the nondestructive testing methods, and have found the applicability. On the other hand, the estimation of content of chloride ions using electromagnetic waves is the average content of chloride ions from concrete surface to rebar, and in order to estimate the distribution of content of chloride ions, it is necessary to decide the surface content of chloride ions and the diffusion coefficient which are set to be equivalent to the average content of chloride ions estimated by electromagnetic waves. In this paper, in order to evaluate the distribution of content of chloride ions during the latency stage and the progression stage before corrosion induced cracks appear on the concrete surface, the method to estimate the distribution of content of chloride ions in the cover concrete combining both electromagnetic waves and X-ray fluorescent is proposed.

1 INTRODUCTION

Salt damage is one of the causes of deterioration of reinforced concrete structures. In addition to the case when chloride ions are mixed in concrete placement, salt damage may penetrate from the surface of concrete by scattering of salt and snow melting agents. In the case of salt damage, if content of chloride ions exceed the limit value of corrosion occurrence in neighborhood of rebar and water and oxygen are supplied, expansion caused by

corrosion of rebar occurs and cracking is generated by the corrosion expansion in the concrete. After that, peeling in the cover concrete and cracking along the reinforcing bar occur on the concrete surface. The peeling and cracks caused by the salt damage do not show any major change until they reach near the surface of the reinforced concrete structure.

In order to evaluate the progression due to salt damage before the occurrence of deformation in the cover concrete, in general,

from the results of chemical analysis such as potentiometric titration using samples obtained by cutting the core drawn out from the target structure at regular intervals in the depth direction, it is possible to investigate the content of chloride ions at that time near the rebar. However, it is difficult to estimate the change over time of the content of chloride ions at the same point with the investigation of the content of chloride ions by the drawn out core, and since it is only possible to investigate the content of chloride ions at the point of drawn core, it is not possible to estimate the degraded part of the target member as an area.

On the other hand, the nondestructive inspection method is a survey to estimate the change of the deterioration situation with the progress of time at the same place without damaging the structure as much as possible. If it is possible to determine the content of chloride ions inside the reinforced concrete structure by this nondestructive inspection method without using the method by coring, it is possible to detect the progress of deterioration due to salt damage at an early stage and it will also be possible to take the countermeasure. When an electrolyte such as sodium chloride is present in concrete, by focusing on the difference in the attenuation of the reflection waveform of the electromagnetic wave from the rebar by the difference in the content of chloride ions, it is possible to estimate the content of chloride ions in the reinforced concrete structure using the electromagnetic wave and authors have been researching and developing for implementation of the method. However, it is confirmed that the attenuation of the reflection waveform of electromagnetic waves changes not only by the change of the content of chloride ions but also by many factors such as the type of cement, material used, mix proportion, temperature and humidity in concrete, cover concrete, surface roughness of concrete. Therefore, it was necessary to propose an equation of estimation that takes these factors into consideration when applying to existing structures[1-3].

In order to solve these subjects, as an estimation evaluation method of the content of

chloride ions using electromagnetic wave, based on the attenuation equation derived from Maxwell's wave equation, the influence coefficients of various factors considered to affect the attenuation of the reflected waveform of the electromagnetic wave were determined from results of the laboratory tests. Based on those results, the equation of estimation of the content of chloride ions using electromagnetic wave was derived by multiplying the conductivity of concrete, which is considered to directly affect the change of content of chloride ions, by the influence coefficients. So far, estimation of the content of chloride ions has been carried out on multiple existing structures using the equation of estimation and the applicability of estimation of the content of chloride ions by electromagnetic waves has been found out[4-5]. However, since the estimation of the content of chloride ions by electromagnetic waves utilizes the attenuation characteristics of the electromagnetic waves, the estimated content of chloride ions itself is the average content of chloride ions from the concrete surface to the position of rebar.

From the above mentions, it is necessary to estimate the content of chloride ions at the rebar position as accurately as possible in order to evaluate the progress of deterioration due to salt damage in the early stage. In order to estimate the content of chloride ions at the position of rebar, for example, the content of chloride ions at the concrete surface is calculated or estimated by another method and it is conceivable to determine the diffusion coefficient using Fick's diffusion equation so that the total content of chloride ions from the surface of concrete to the position of the rebar becomes equivalent to the average content of chloride ions estimated by the electromagnetic wave[6-8]. However, when chloride ions migrate into concrete due to the influence of carbonation etc., it is difficult to estimate the content of chloride ions at the position of rebar by applying the Fick's diffusion equation.

Therefore, as a method for estimating the distribution of content of chloride ions, the authors measured with the handy type fluorescent X-ray analyzer using drilling

powders with the small diameter drill machine from the structure to be surveyed and it was conducted to study the method for estimating the distribution of chloride ions easily in the field. Although the estimation accuracy of the method for estimating the content of chloride ions using this handy-type fluorescent X-ray analyzer has been confirmed in previous researches[9-10], since there have been few application examples in existing structures using this method, in order to confirm whether the existing structure is sufficiently applicable, 861 samples are collected from 120 locations at 8 sites and compared with the potentiometric titration method, and the comparison was carried out with respect to the apparent diffusion coefficient and surface content of chloride ions estimated from the distribution of content of chloride ions by fluorescent X-ray. Using the apparent diffusion coefficient and the position of the maximum content of chloride ions inside the concrete estimated from the distribution of content of chloride ions by this fluorescent X-ray, the maximum content of chloride ions is determined so as to be equivalent to the total content of chloride ions calculated from the average content of chloride ions to the position of rebar estimated using electromagnetic waves and in addition to estimating the content of chloride ions at the position where the content of chloride ions reached or the position of rebar, the method was proposed to create a mapping to assess the degradation progress due to salt damage at the survey field.

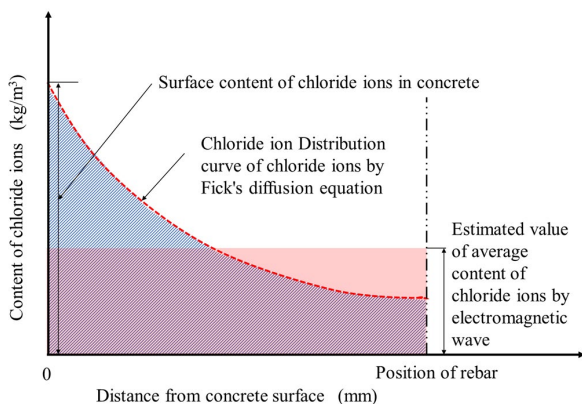


Figure 1 Relationship between chloride ion distribution and average content of chloride ions

In this paper, as the method to easily estimate the penetration of chloride ion into concrete in the survey field for the purpose of early detection of deterioration caused by salt damage, by combining the estimation results of the average content of chloride ions up to the position of rebar by the nondestructive inspection using electromagnetic waves and the estimation result of the distribution of content of chloride ions using fluorescent X-ray analysis, the method is proposed to estimate the distribution of chloride ions on the surface of concrete as a plane and the results of applying the method to the existing structure are reported.

2 DISTRIBUTION OF CONTENT OF CHLORIDE IONS BY ELECTROMAGNETIC WAVES

2.1 Estimation method using electromagnetic waves

The content of chloride ions estimated using electromagnetic waves is the average content of chloride ions from the concrete surface to the position of rebar and does not indicate the content of chloride ions at the position of rebar. However, it can be assumed that the total content of chloride ions in the cover concrete is theoretically equivalent to the value obtained by multiplying the depth of cover concrete by the average content of chloride ions obtained by electromagnetic waves.

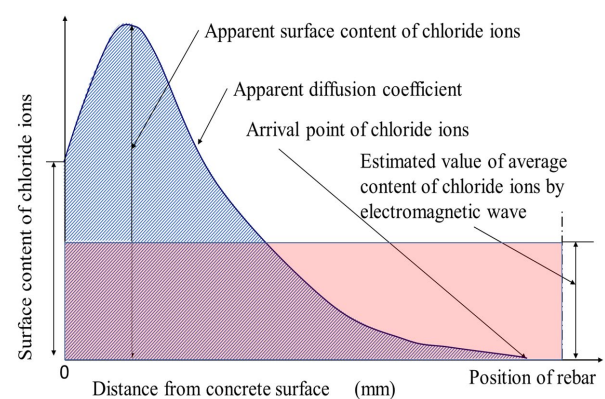


Figure 2 Chloride ion distribution when no chloride ion has reached the rebar position

Therefore, assuming that the distribution of content of chloride ions in the cover concrete is the distribution shown in Fig. 1 in a concrete structure that has passed a certain age, for example, if the surface content of chloride ions and diffusion of concrete in the Fick's diffusion equation can be determined to be equal to the total content of chloride ions in the cover concrete, it is possible to estimate the content of chloride ions at the position of rebar. However, the number of combinations of surface content of chloride ions and diffusion coefficient of concrete, which is equal to the total content of chloride ions, is innumerable and the solution itself becomes indefinite. Therefore, in order to make the estimated distribution of content of chloride ions equal to the total content of chloride ions in the cover concrete estimated by electromagnetic waves, it is necessary to determine either the surface content of chloride ions or the diffusion coefficient of concrete. In addition, as shown in Fig. 2, when the content of chloride ions has not reached the position of rebar, or when the position of the maximum content of chloride ions has shifted to the inside of the concrete due to carbonation etc., it is necessary to determine the total content of chloride ions in consideration of these conditions.

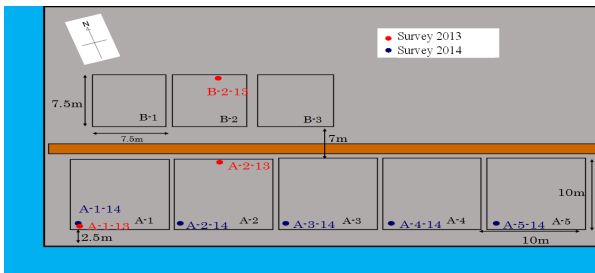


Figure 3 Outline of sampling points

In this study, for each case where the content of chloride ions has not reached the rebar position and the content of chloride ions has reached the position of rebar, the estimation method is proposed in which the estimated distribution of chloride ions is equivalent to the total content of chloride ions up to the position of rebar using the average content of chloride ions obtained by

electromagnetic waves. When the maximum content of chloride ions is shifted to the inside of the concrete due to carbonation etc. as shown in Fig. 2, the maximum content of chloride ions was defined as the apparent surface content of chloride ions and it was assumed that the apparent diffusion coefficient was obtained from the distribution of content of chloride ions below based on the apparent content of surface chloride ions.

2.2 Apparent surface content of chloride ions and apparent diffusion coefficient

The distribution of content of chloride ions in the surveyed fields obtained by potentiometric titration etc. differed depending on the service life, environmental conditions such as wind direction and distance from the sea, direction of drawn cores (upper surface, side surface, and lower surface), etc. As an example, in the deterioration survey on the piers of the coal-fired thermal power station carried out about 15 years after service shown in Fig.3, the measurement results of the content of chloride ions by potentiometric titration at different sampling points are shown in Figure 4, 5. As the results of chemical analysis, the content of chloride ions in the A-1 block closest to the sea was high and in the B-2 block located about 25 m away from the sea, the surface content of chloride ions was 1/6 or less of that in the A-1 block. In addition, in the A-4 and A-5 blocks located at the same distance from the sea surface on the south side and far from the sea surface on the west side with respect to the A-1 whose two sides are surrounded by sea, since the surface chloride ion amount is about 1/3, it seems that differences occur in the penetration of the content of chloride ions into the concrete even on the same pier. On the other hand, the apparent diffusion coefficient estimated based on the measurement results of the content of chloride ions was almost the same value at each survey position.

Therefore, even if the apparent surface content of chloride ions is relatively close, it is considered to be greatly different depending on environmental conditions etc.. On the other

hand, the apparent diffusion coefficient shows almost the same estimated value at each sampling point, and if the mixing conditions and the construction time are the same at the surveyed structure, it seems that the influence of differences in sampling point is small.

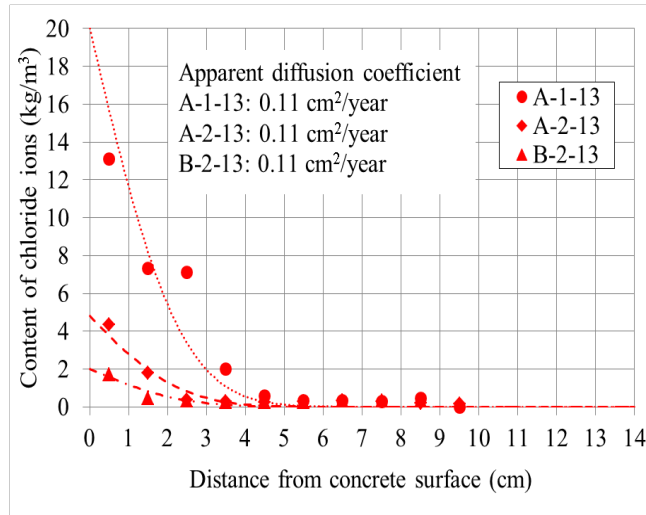


Figure 4 Chloride ion distribution (2013 survey)

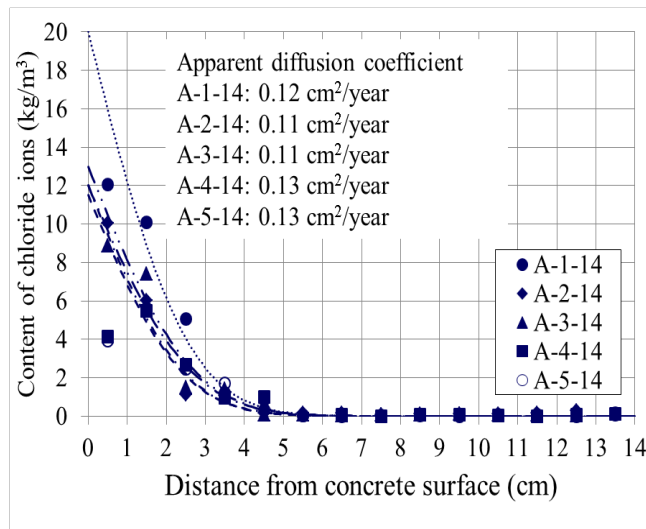


Figure 5 Chloride ion distribution (2014 survey)

In this paper, the apparent diffusion coefficient is used as a constant in estimating the distribution of content of chloride ions, the apparent surface content of chloride ions is used as a variable, and the apparent surface content of chloride ions was determined so as to be equivalent to the total content of chloride ions up to the position of rebar calculated from the estimation results by the electromagnetic waves.

3 ESTIMATION OF CONTENT OF CHLORIDE IONS USING PORTABLE X-RAY FLUORESCENCE ANALYZER

3.1 Estimation of distribution of content of chloride ions by combination of small diameter drill machine and portable X-ray fluorescence analyzer

In order to estimate the distribution of content of chloride ions using the average content of chloride ions estimated by electromagnetic waves, as described above, it is necessary to determine the apparent diffusion coefficient and the position when the maximum content of chloride ions has shifted to the inside of the concrete due to carbonation etc.. The authors have collected samples with core drills at the surveyed fields and have determined them based on the chemical analysis results by potentiometric titration. However, since the method of drawn cores has problems such as that it takes time for sampling and cutting, crushing and pretreatment for chemical analysis after sampling take time and cost, it is difficult that the mapping of the content of chloride ions can't be performed in a short time. Therefore, using the combination method of sampling by small diameter drill machine and analysis due to the fluorescent X-ray analyzer, which has many past research results and its usefulness has been confirmed, in order to estimate the distribution of content of chloride ions at the survey fields, it was carried out to determine the apparent diffusion coefficient and the position when the maximum content of chloride ions has shifted to the inside of the concrete due to carbonation etc..

The fluorescent X-ray analyzer includes the wavelength dispersive type using the dispersive crystal and the energy dispersive type using the semiconductor detector. Although the energy dispersive type is inferior to the wavelength dispersive type in wavelength resolution performance and detection sensitivity, it is possible to analyze a large number of elements simultaneously and in a short time and as the apparatus itself is inexpensive and compact, the device is suitable for measurement in the site. In this

study, samples were collected using a small diameter drill machine and measurements were made using drilling powder using the energy dispersive portable X-ray fluorescence analyzer and the method was applied to estimate the content of chloride ions in concrete from the calibration curve prepared in advance.

In this method of sampling with the small-diameter drill machine and estimating the content of chloride ions using the portable X-ray fluorescence analyzer, it is possible to analyze with a very small amount (about 2 to 5 g) compared to the method by drawn cores and as in the case of potentiometric titration, it is not necessary to perform pretreatment for chemical analysis and the measurement time is short (about 2 minutes). In addition, since the amount of sample collection is several tenths of that in the case of drawn cores, damage to the structure is much smaller than in that of drawn cores. Furthermore, because of the small diameter, it is possible to sample in the vicinity of the rebar in comparison with the case of drawn core and if the depth of cover concrete is accurately measured, since it is possible to sample directly on the rebar, it also is possible to measure the content of chloride ions in the vicinity of the rebar. The equipment used itself is lighter than the core drill machine, and since time and labor for fixing the core drill machine is not required, for example, even at the place where sampling can't be performed unless the scaffold such as the lower surface of the slab in the pier is installed, it is possible to sample from the ship.

On the other hand, in the case of sampling using the small diameter drill machine, since the amount of sampling is small, there is a problem that the variation at the time of measurement becomes large. Therefore, in order to reduce the variation during measurement, it is necessary to collect a plurality of samples at the same place. In this study, regarding the estimation of the content of chloride ions by X-ray fluorescence analysis, using samples collected from 120 locations with small diameter drill machine in existing structures at 8 survey fields that differ in materials used, environmental conditions,

years of service life, structure type, and direction of the collection (upper surface, side surface, lower surface), it was investigated to evaluate the measurement accuracy with the fluorescent X-ray by comparing the results of measurement by X-ray fluorescence and the results of chemical analysis by potentiometric titration and the applicability was investigated regarding the apparent diffusion coefficient calculated from the results of measurement of X-ray fluorescence.

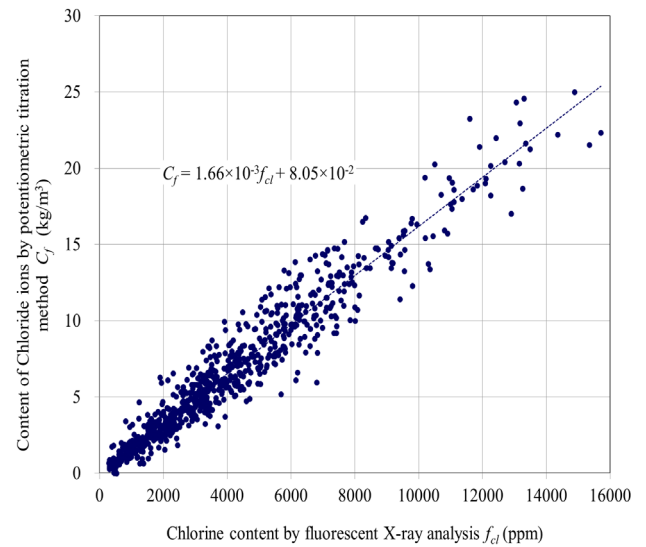


Figure 6 Relationship between the content of chlorine by fluorescent X-ray analysis and the content of chloride ions in concrete

3.2 Estimation results of distribution of chloride ions by X-ray fluorescence analysis

In this study, sampling for estimation of the amount of chloride ion by X-ray fluorescence analysis was carried out to 8 different places in 5 facilities of coal-fired thermal power station, 2 bridges and 1 facility of steel mill. The sampling points are 120 places of lateral side of girder 84 places, bottom side of girder 9 places, upper side of girder 1 place, beam side 7 places, beam bottom 10 places and bottom of slab 9 places. The drilling powder was collected in 1 cm interval at each location and the sampling depth was 5 cm to 12 cm. The years of service in the structures at the time of the survey were 27 to 37 years. The content ratio of chlorine was measured using an energy dispersive

portable fluorescent X-ray analyzer for all 861 samples collected and at the same time, the content of chloride ions was analyzed by potentiometric titration. Based on the measurement results and analysis results, the relational equation between the chlorine content ratio f_{cl} (ppm) by fluorescent X-ray analysis and the content of chloride ions C_f (kg / m^3) was determined. The relational equation is shown below and shown in Fig.6.

$$C_f = 1.66 \times 10^{-3} f_{cl} + 8.05 \times 10^{-2} \quad (\text{kg/m}^3) \quad (1)$$

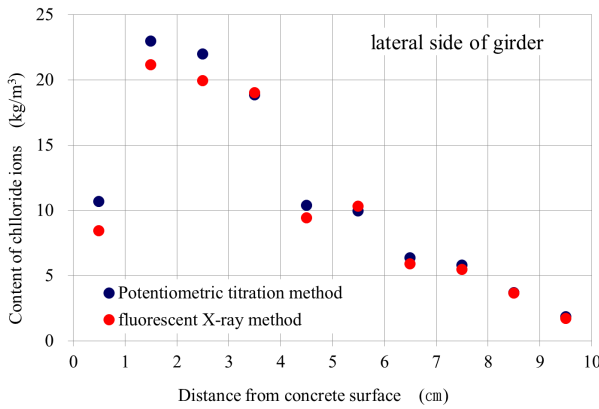


Figure 7 Comparison of the estimation results by X-ray fluorescence analysis and the analysis results by potentiometric titration

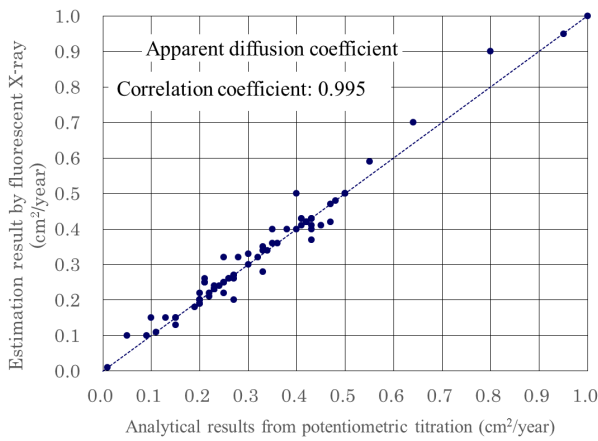


Figure 8 Comparison of apparent diffusion coefficients

From Fig. 6, although the construction site, the service life, and the sampling site are different, the relatively high correlation (correlation coefficient 0.967) was confirmed between them. Fig.7 shows an example of the result of comparing the distribution of chloride ions estimated from the X-ray fluorescence analysis results using equation (1) with the

distribution of chloride ions obtained by potentiometric titration method. From Fig. 7, although the distribution of content of chloride ions estimated from results of the X-ray fluorescence analysis has a little difference at each position with respect to the distribution of content of chloride ions obtained by potentiometric titration method, both showed almost the same distribution.

As shown in Fig.8, the apparent diffusion coefficient confirmed the high correlation between the value obtained from the estimation result by X-ray fluorescence analysis and the value obtained from potentiometric titration. Therefore, it was judged that the apparent diffusion coefficient estimated from results of the X-ray fluorescence analysis can be applied to the equation for estimating the content of chloride ions at the position of rebar from the average content of chloride ions estimated by the electromagnetic waves. In addition, as shown in Fig.9, since the high correlation was also recognized between the values for the apparent surface content of chloride ions, it was judged that the estimation results by X-ray fluorescence analysis could be applied.

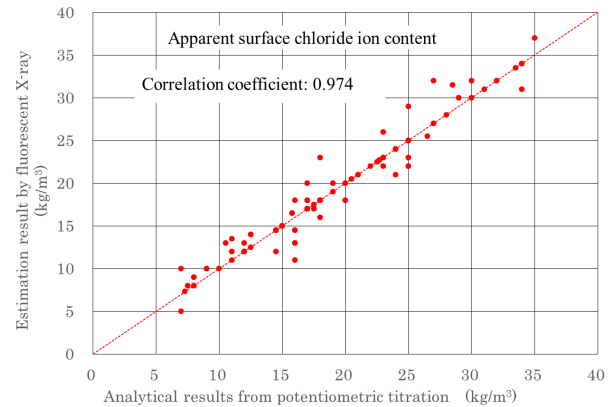


Figure 9 Comparison of apparent surface content of chloride ions

From the above results, in this study, in the estimation of the distribution of the content of chloride ions using electromagnetic waves in existing structures, with regard to the apparent diffusion coefficient and the point of the maximum content of chloride ions, it was decided to apply the value calculated from the

estimation results of the fluorescent X-ray analysis.

4 MAPPING OF CHLORIDE IONS

Based on the results of previous studies, an application example of the mapping of content of chloride ions in reinforced concrete combining electromagnetic waves and fluorescent X-rays to existing structures is shown below.

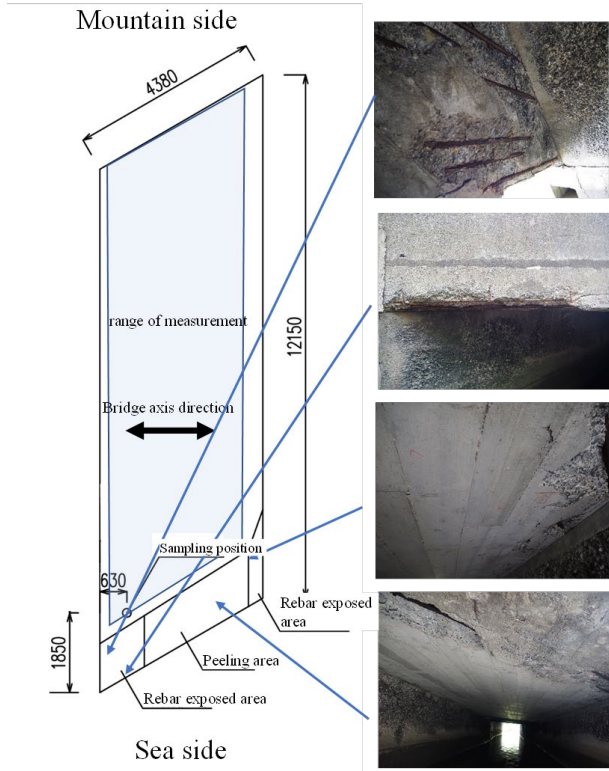


Figure 10 Appearance status and measurement range of survey field

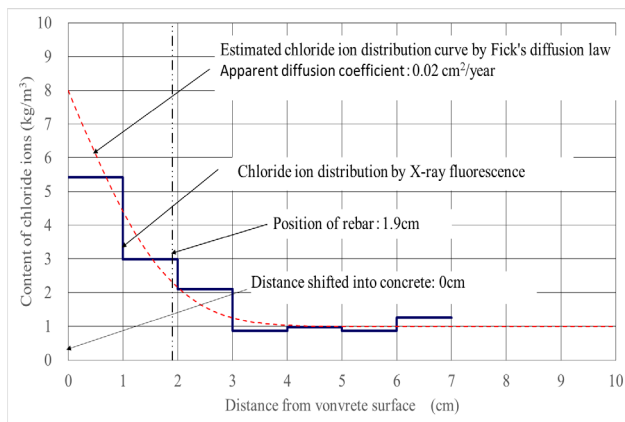


Figure 11 Chloride ion distribution by X-ray fluorescence analysis

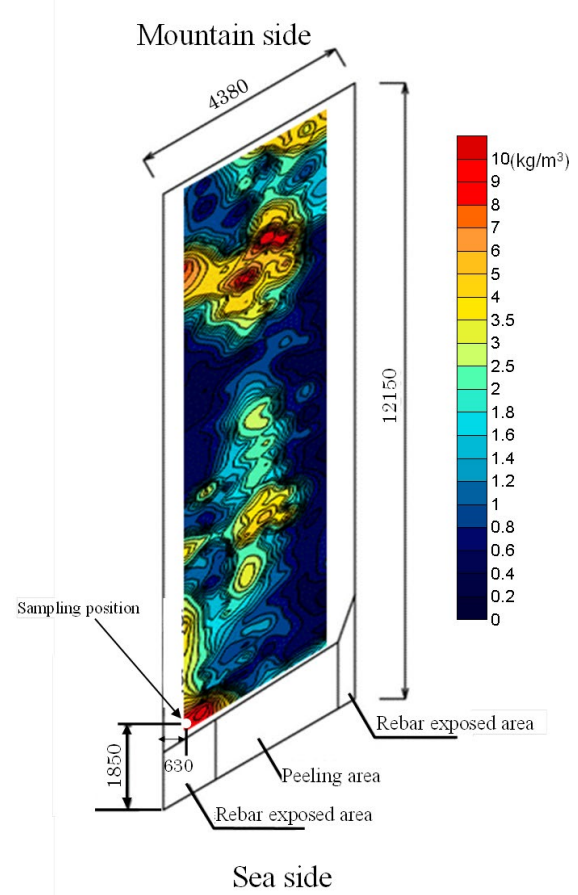


Figure 12 Distribution of chloride ion at position of rebar

The surveyed structure is the bridge constructed at a distance of about 50 m from the coast and it has been 57 years since its service. The survey point is the bottom of reinforced concrete floor slab. As shown in Fig. 10, the peeling of concrete has occurred in the range of about 1 m from the end facing the coast, and the rebar is exposed in the exfoliated concrete. On the other hand, almost no cracks were observed inside the floor slab and no peeling concrete was almost observed. As shown in Fig. 10, measurements were carried out using electromagnetic waves around the inside of the undamaged floor slab and at the point relatively close to the location where chloride ions penetrate and are damaged, it was carried out to collect by the small diameter drill machine and to estimate the amount of chloride ion by X-ray fluorescence analysis. The estimation results by X-ray fluorescence analysis and the apparent diffusion coefficients calculated based on the

estimation results are shown in Fig.11. As for the position of the maximum content of chloride ions, since the migration to the inside of the concrete due to the carbonation etc. was not confirmed, in this study, the position of the maximum content of chloride ions was used as the concrete surface. Figure 12 shows the mapping based on the estimation results of the content of chloride ions at the position of rebar from the 318 measurement points using the calculated apparent diffusion coefficient.

From Fig. 12, the area where the content of chloride ions at the position of rebar is less than $1.2 \text{ kg} / \text{m}^3$ is about 50% and the area less than $2.4 \text{ kg} / \text{m}^3$ is about 80%. Assuming that the limit value of corrosion initiation is in the range of $1.2 \text{ kg} / \text{m}^3$ to $2.4 \text{ kg} / \text{m}^3$, although 50 to 80% of the bridge decks surveyed have been in use for about 60 years, the content of chloride ions at the position of rebar may not exceed the limit value of corrosion initiation. Although it may be judged that the target bridge is deteriorating from damage due to salt damage on the sea side, the visual inspection of appearance of structure and years of service, from estimation results of this survey, it is estimated that corrosion of rebar does not occur in many parts of the target bridge.

5 CONCLUSIONS

In this paper, for the purpose of early evaluating the progress of deterioration due to salt damage of reinforced concrete structures, a method was proposed for the penetration of content of chloride ions into concrete and the estimation of content of chloride ions at the position of rebar simply in the survey field. The method proposed in this paper is to estimate the content of chloride ions at the position of rebar by changing the apparent surface content of chloride ions so that the total content of chloride ions in the area covered by electromagnetic waves and the content of chloride ions estimated by X-ray fluorescence analysis become equivalent from the results of the average content of chloride ions in the cover concrete by electromagnetic waves and the distribution of chloride ions obtained by portable X-ray fluorescence

analysis using drilling samples by small diameter drill machine,

From the results of applying the mapping of the content of chloride ions at the position of rebar in reinforced concrete combining electromagnetic waves and fluorescent X-ray analysis to the existing structures, in the stage where almost no deformation is observed on the concrete surface, it is possible to find out the applicability of this method as an estimation method for evaluating the progress of deterioration.

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