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A STUDY ON THE PROTECTION OF STEEL IN CONCRETE BY PENETRATIVE CORROSION INHIBITOR·

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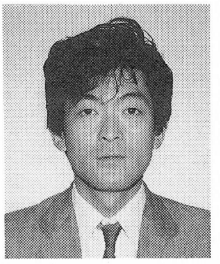

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SYNOPSIS

Concrete structures are damaged by the corrosion of reinforcing bars due to chlorides in concrete, when cover thickness is not sufficient, or when the quality of concrete is poor.

Therefore they often need repair even at early stage of their life span. This paper described that coating of concrete surface with a corrosion inhibitor, which spreads into concrete by diffusion, is an effective repair method. In this study, corrosion tests were conducted taking such factors as NO_2/Cl^- ratio and NO_2^- diffusion.

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1. INTRODUCTION

Salt damage to concrete structures can be broadly classified into the following two:

(1) Damage caused by chloride having entered concrete during construction:

Corrosion of reinforcing bars resulting from the use of inadequately desalted sea sand and the heavy use of calcium chloride based additives.

(2) Damaged caused by chloride having entered concrete from outside after construction:

Corrosion of reinforcing bars due to chloride derived from sea salt particles adhering to concrete surfaces and infiltrating into concrete as a result of repeated wetting and evaporation and diffusion when the structure is located under marine environment, and the corrosion of reinforcing bars caused by chloride in concrete as a result of the use of deicer.

A salt damage preventive measure has been recently developed primarily in the U.S.. Under this measure, a large amount of a high performance rust preventive is added to concrete beforehand, to prevent the corrosion due to the infiltration of chloride. Two application examples of this method have been reported[1][2]. The rust prevention mechanism of corrosion inhibitor which is the main component of a high performance rust preventive is as follows: NO_2^- ions act on Fe^{2+} ions as shown in the formula below. Such mechanism[3] prevents the move of Fe^{2+} ions from the anode part, causing them to deposit on metal surfaces as Fe_2O_3 consequently forming impermeable passive film and prevent the corrosion of reinforcing bars.

$$2F^{2+} + 2OH^- + 2NO_2^- \longrightarrow 2NO + Fe_2O_3 + H_2O \quad ....(1)$$

However, following problems may be caused by the addition of a large quantity of calcium nitrite[4] which is the main component of a high performance rust preventive.

(1) Economically, concrete cost will increase by 20 to 25%.

(2) Slump loss will become greater, which cause a decline in workability because such addition will accelerate the development of initial concrete strength. To solve these problems effectively, the authors presented a method in which corrosion inhibitor is applied to concrete surfaces after construction. In this method, the corrosion inhibitor permeate the concrete around the reinforcing bars through density-diffusion, consequently corrosion is prevented. In this paper, the following have been made clear.

(1) Necessary molar ratio between NO_2^- and Cl^- in concrete to prevent the corrosion of reinforcing bars.

(2) Infiltration of corrosion inhibitor into concrete through density-diffusion.

(3) Anticorrosion effects.

(4) Suitability to actual structures and follow-up research.

Prevention of corrosion of reinforcing bars by the application of corrosion inhibitor.

In considering the prevented of corrosion of reinforcing bars by applying corrosion inhibitor which infiltrates into concrete through density-diffusion, attention may be paid to following examination:

(1) When corrosion inhibitor is mixed into concrete, the standard NO_2^-/Cl^- mole ratio effective to prevent corrosion is 0.82[5][6]. Mole ratio greater than this value shall be used.

(2) Attention must be paid to a difference in mole ratio the conditions of corrosion of reinforcing bars and the Cl^- concentration around reinforcing bars.

(3) It is necessary to check the existence cracks in concrete surfaces and their width that are considered to have a significant effect on permeability.

2. ANTICORROSION EFFECTS ON RUST-FREE REINFORCING BARS

2.1 Outline of tests

The mix proportion of concrete is presented in Table 1.

Table 1 Mix proportion of concrete

W/C (%)	S/a (%)	Air content (%)	Slump (cm)	Quantity of material per unit volume of concrete (kg/m^3)			
				W	C	S	G
70	50	3.6	15.6	173	247	932	938

The details of specimen are shown in Fig. 1. A 10mm in dia. x 100mm could finished steel bar specified in JISA 6205 was embedded in the 10mm position for covering.

After coating penetrative corrosion inhibitor to the underside of the chloride-contained specimen (with rust-free reinforcing bars), we performed four cycles of accelerated corrosion tests using autoclave and studied NO_2^-/Cl^- mole ratio and anticorrosion effects.

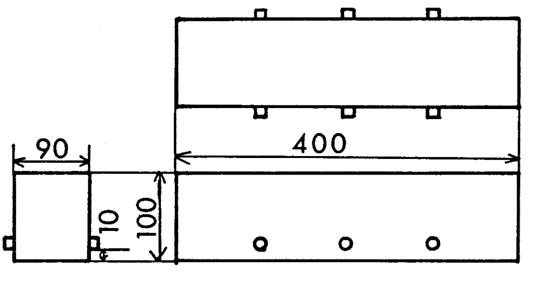


Fig. 1 Details of specimens (mm)

2.2 Test results

Necessary ratio of NO_2^-/Cl^- mole ratio to obtain anticorrosion effects are estimated to be about 0.6 to 0.7 as shown in Fig. 2. Increase of mole ratio does not necessarily occur with increase of Cl^- the mole ratio was smaller than 0.82 which was considered to be the mole ratio effective to prevent corrosion when corrosion inhibitor was mixed in. Thus, however test results did not fully demonstrate the relationship between the mole ratio and anticorrosion effects due to the following:

This was because NO_2^- had a high solubility, and submersion in water at high pressure in an autoclave, in particular, caused NO_2^- ions to accumulate near the reinforcing bars located 2cm inside from concrete surfaces as shown in Fig. 3. As a result, it appears that NO_2^-/Cl^- mole ratio became smaller than the value necessary to obtain anticorrosion effects.

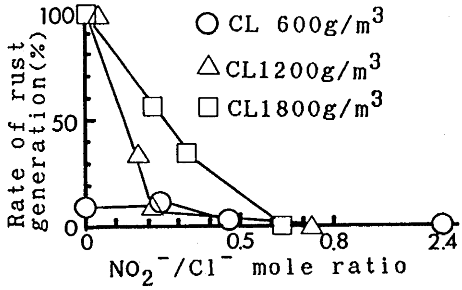


Fig. 2 Anti-corrosion effects

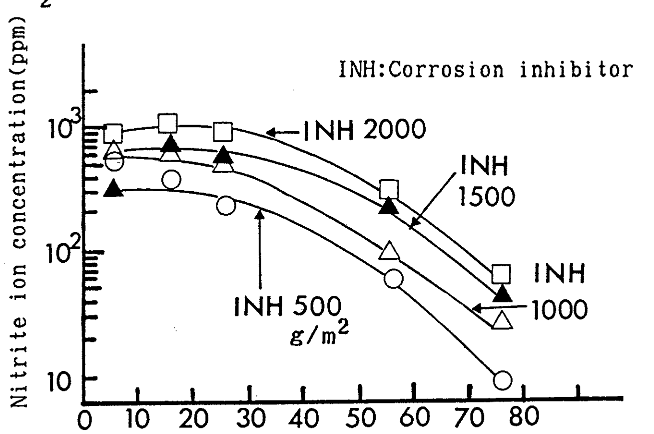


Fig. 3 Relationship between the nitrite ion concentration and the depth from the concrete surface in specimens

3. ANTICORROSION EFFECTS ON REINFORCING BARS ALREADY SUFFERED FROM CORROSION

3.1 Outline of tests

The formulation of concrete and the shape of the specimen are described in 2.1. We used reinforcing bars already suffering from about $32 mg/cm^2$ corrosion caused by the repeated wetting and drying of salt. We mixed NaCl into concrete so that Cl^- ion in concrete became 0, 600, 1,200 and $1,800 g/m^2$.

The specimen were cured in the room for a month after having been coated with the prescribed quantity of corrosion inhibitor from the covering side. Then, we performed four cycles of accelerated corrosion test, with a combination of autoclave and submersion taken as one cycle.

After accelerated corrosion tests, we performed the quantitative determination of NO_2^- and evaluated its permeability. Anticorrosion effects were examined through the measurement of decrease in corrosion and corrosion depth.

3.2 Test results

The results, especially the relationship between NO_2^-/Cl^- mole ratio and decrease in corrosion are shown in Fig. 4.

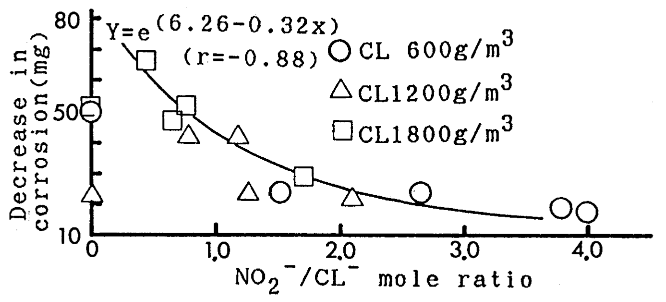


Fig. 4 NO_2^-/Cl^- mole ratio and decrease in corrosion

As can be seen from the figure, an exponential relationship exists between decrease in corrosion and NO_2^-/Cl^- mole ratio. The relationship can be expressed by the following equation:

$$y = e^{6.26 - 0.31x} \quad ....(2)$$

Correlation coefficient r = 0.88 where
y : decrease in corrosion
x : NO_2^-/Cl^- mole ratio

The exposure of a 5mm portion from the both edge of the specimen. Therefore, when seen from the 20mg position on axis y, the NO_2^-/Cl^- mole ratio to obtain anticorrosion effects will be about 1.8 to 2.0.

That is, mole ratio necessary to prevent further corrosion of already corroded reinforcing bars is far greater than the test results obtained in 2.1.

This means that if reinforcing bars has already corroded, NO_2^- ions diffuse in corrosion sediment and permeate to reach corrosion-free reinforcing bars surfaces. NO_2^- ions then act on easily isolatable Fe^{2+}, forming a passive film to prevent the further development of corrosion.

4. PERMEABILITY AND ANTICORROSION EFFECTS IN A CRACK

4.1 Outline of tests

To investigate the permeability of corrosion inhibitor into a crack and the anticorrosion effects on reinforcing bars, we prepared a specimen based on the factors and standards shown in Table 1, Fig. 5, Fig. 6, Fig. 7 and applied corrosion inhibitor to the specimen to which we then atomized artificial sea water as to accelerate corrosion.

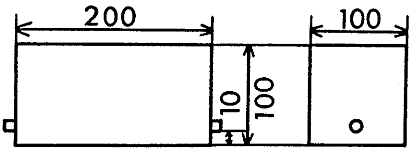
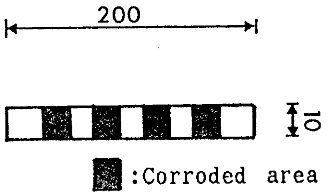


Fig. 5 Details of specimens (mm)



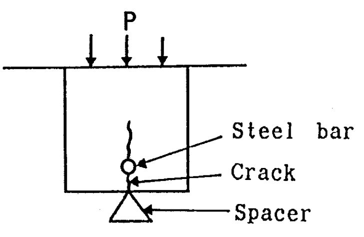


Fig. 7 Method for initiating cracks

Fig. 6 External appearance of partly corroded steel bar

Corroded area

After a crack has occurred in the specimen, we applied the prescribed quantity of nitrite to the specimen by brushing downward.

Thereafter, the specimen was left to stand in a constant temperature room at 20°C and at the humidity of 50% for thirsty days.

Corrosion was accelerated in the room by atomizing artificial sea water to the cracked surfaces placed to face up once a week during a one year period.

After accelerated corrosion promotion tests, we performed the quantitative determination of NO_2^- ions to evaluate its permeability. Anticorrosion effects were examined through the measurement of decrease in corrosion and corrosion area.

4.2 Test results

(1) Permeability of corrosion inhibitor into a crack

NO_2^- ion concentration distribution in a crack is shown in Fig. 8. As is apparent from the figure, the greater the crack width and the crack width and the volume applied, the deeper the corrosion inhibitor permeated into the specimen.

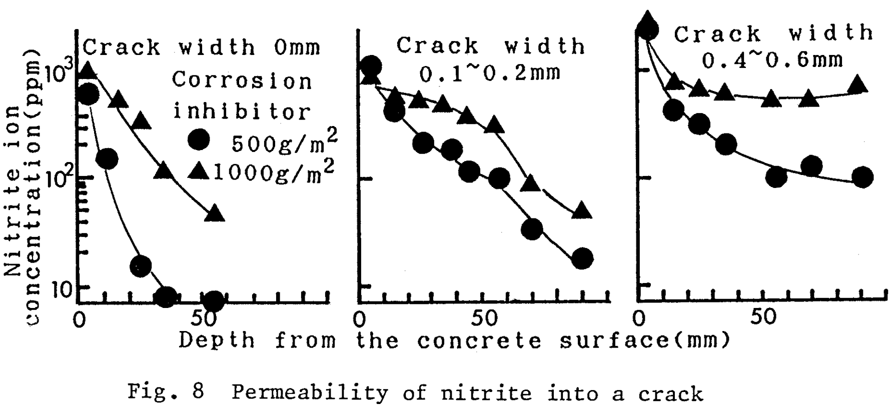


Fig. 8 Permeability of nitrite into a crack

(2) Anticorrosion effects of corrosion inhibitor on a crack

The relationship between the NO_2^-/Cl^- mole ratio and corrosion area ratio in a crack is shown in Fig. 9. Corrosion area ratio increased sharply when crack width exceeded 0.1 to 0.2mm.

There was no significant difference in the anticorrosion of reinforcing bars whether Cl^- ions are mixed in or not. Therefore, even when about 1,200g/m^2 chloride ions are mixed in, a large portion of Cl^- ions are fixed as Friedel's salt. For this reason, in the case of corroded reinforcing bars in concrete with a crack of about 0.1 to 0.2mm in width, the development of corrosion is considered to be preventable through the application of 1,000g/m^2 corrosion inhibitor.

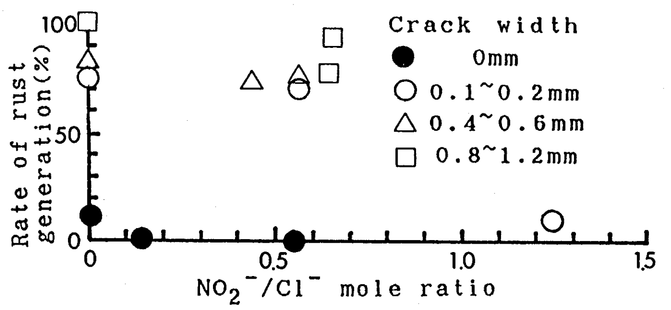


Fig. 9 Anti-corrosion effects of corrosion inhibitor on crack

5. APPLICATION EXAMPLES OF A CORROSION INHIBITOR TO ACTUAL STRUCTURES

5.1 Application examples after the one year experiment

To see the permeability of the corrosion inhibitor and its anticorrosion effects on reinforcing bars, an on-site application test was performed in order to study the volume of corrosion inhibitor to be applied and its application method using overbridge deck constructed more than 15 years ago.

When the outside appearence examination of the deck structure was performed prior to the implementation of the on-site application test, no marked cracks except for local rust stains were discovered.

According to the analysis of salt in concrete, Cl^- ions on the underside of deck that were considered to be introduced from the use of inadequately desalted sea sand accounted for 0.08% (Cl^- ions mixed in concrete: about 1,800g/m^2) when all the salt content was converted into Cl^- ions.

This value indicated a high salt content that is three times the permissible salt content for RC structures specified by the Japan Civil Engineering Society.

We applied 1,000g/m^2 of 0.5 NO_2^-/Cl^- mole ratio corrosion inhibitor to partial surface of the deck, by brushing from below five to seven times.

NO_2^- infiltration results during a one year period following the application is shown in Fig. 10. After application, as time went by, NO_2^- ion density-distribution, its permeability is considered to be favorable.

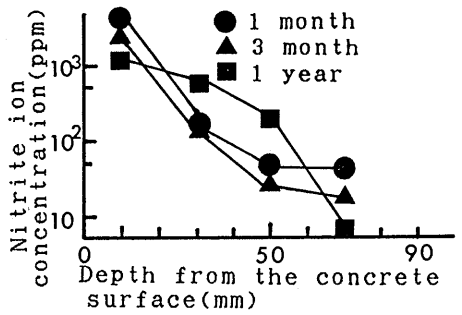


Fig. 10 NO_2^- infiltration results

5.2 Diffusion of NO_2^- ions into concrete

Apparent diffusion volume at each age D' (mm^3) was calculated by apparent diffusion equation and plotted as shown in Fig. 11 by substituting NO_2^- ions concentration, apparent diffusion coefficient Dc (mm^3/day) and surface density Co (ppm). The diffusion coefficient is derived from the primary regression line and a different method of application by use of press-fitting method is also summarized for comparison purposes in Fig. 11.

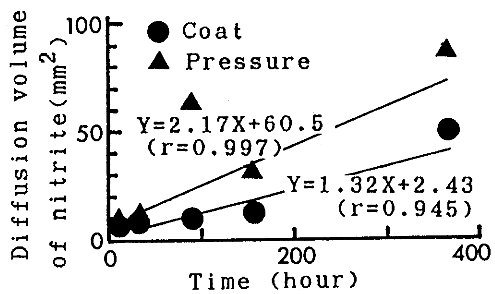


Fig. 11 Diffusion of nitrite

6. CONCLUSIONS

Results obtained in this thesis can be concluded as follows:

(1) The NO_2^-/Cl^- ratio required for the concrete with corroded steel is twice as high as that for the concrete without corroded steel.

(2) The application of penetrative coating with NO_2^-/Cl^- ratio increased to 1.82 will eliminate an adverse effect of Cl^- successfully even for the concrete with corroded steel.

(3) Outstanding anticorrosion effects were identified in a crack of 0.1 to 0.2mm in width. In this case, NO_2^-/Cl^- mole ratio is considered to be about 1.5.

(4) Degree of penetration or diffusion of corrosion inhibitor were confirmed in the actual large scale structures successfully. We also experimented the electrical Halfcell Potential and Polarization Resistance method to monitor anticorrosion effects produced by the application of corrosion inhibitor.

7. REFERENCES

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