ELSEVIER

Cement & Concrete Composites 25 (2003) 123–129

Cement & Concrete Composites

www.elsevier.com/locate/cemconcomp

Repair materials system for chloride-induced corrosion of reinforcing bars

H. Tatematsu [a,*], T. Sasaki [b]

[a] Railway Technical Research Institute, Planning Division, Hikaricho, Kokubunnji City, Tokyo, Japan
[b] Railway Technical Research Institute, Materials Technology Division, Hikaricho, Kokubunnji City, Tokyo, Japan

Accepted 31 July 2001

Abstract

Chloride-induced corrosion of reinforcement is a serious problem that threatens the durability and strength of concrete structure. In order to suppress the corrosion of reinforcing bars, a salt adsorbent was chemically synthesized which could adsorb excess amounts of chloride ions and release nitrite ions. Large-size specimens partly repaired with mortars containing the adsorbent were exposed to a natural environment. It was found that the reinforcing bars have been varied to a sufficiently high-level passivation state. We call a new repair method established by using these corrosion inhibitors of the salt adsorbent, suppressing salt injury method (SSI method). The method was applied to actual concrete railway structures. The structures which were repaired by the SSI method have been maintained at a sound state.

Keywords: Chloride-induced corrosion; Reinforcing bar; Repair; Salt adsorbent; Chloride ion; Nitrite ion

1. Introduction

Extensive researches [1–3] are being promoted on the countermeasures for reinforcing bar corrosion caused by salt because such corrosion seriously affects the durability and strength of concrete structures. To protect concrete structures from damages by chloride-induced corrosion, concrete surfaces are treated with water-impenetrable materials to prevent the penetration of salt and water from the outside. Such treatment can be performed easily at a relatively low cost. Even after treatment, however, the salt in concrete remains behind, and the water content of concretes often increases, resulting in acceleration of the deterioration of concrete. To completely suppress the damages caused by chloride-induced corrosion, it is desirable to extract salt from concrete as much as possible.

In this study, first of all, we chemically synthesized a salt adsorbent that could adsorb chloride ion (Cl^-) and release nitrite ion (NO_2^-), leading to the suppression of reinforcing bar corrosion. Secondarily, to confirm the corrosion inhibiting effect of the salt adsorbent, we prepared large-size specimens repaired with the corrosion inhibiting materials containing the salt adsorbent, and then subjected them to a long-term exposure test. Based on the successful result of the exposure test, we developed the repair system of suppressing salt injury method (SSI method) by using the materials containing the salt adsorbent.

This paper reports the corrosion inhibiting effect of the salt adsorbent confirmed through the exposure test carried out by using large-size specimens and their application to actual concrete railway structures.

2. Synthesis of salt adsorbent

To suppress the chloride-induced corrosion of reinforcing bars, it is effective to fix and deactivate chloride ions in concrete. Chemically synthesized nitrite type hydrocalmite [4] is expected to behave as an anion exchanger to adsorb the chloride ion. This material is referred to as "salt adsorbent" in the following. Fig. 1 shows a schematic view of the structure of the material.

---

[*] Corresponding author. Tel.: +81-42-573-7230; fax: +81-42-573-7209.

E-mail address: tatematu@rtri.or.jp (H. Tatematsu).

0958-9465/03/$ - see front matter © 2002 Published by Elsevier Science Ltd.
PII: S0958-9465(01)00059-2

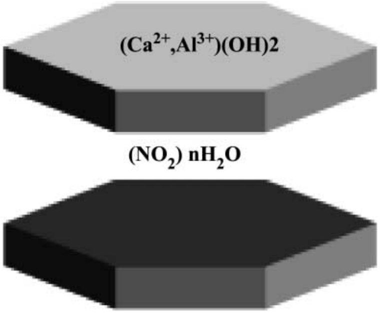

Fig. 1. Schematic structure of the salt adsorbent.

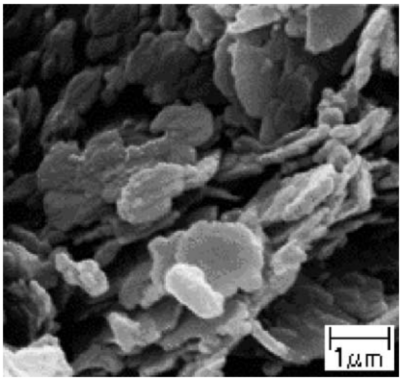

Fig. 2. SEM image of the salt adsorbent.

A scanning electron microscopic (SEM) image of the salt adsorbent is given in Fig. 2.

In the crystal structure of the salt adsorbent, a part of calcium ions (Ca^{2+}) are substituted by aluminum ions (Al^{3+}) in the calcium hydroxide layer $Ca(OH)_2$ importing an excess positive charge to the layer. An amount of anion had to be introduced in the interlayer space to compensate for the positive charge. As the anion species to compensate for the positive charge on the layer, nitrite ion was chosen because of its characteristics to suppress reinforcing bar corrosion. In contact with chloride ions, this material adsorbed the chloride ions releasing the nitrite ions following the ion exchange reaction as shown by the following Eq. (1).

$$\underset{\text{(Nitrite type hydrocalmite)}}{3CaO\ Al_2O_3\ Ca(NO_2)_2\ nH_2O} + 2Cl^- \rightarrow 3CaO\ Al_2O_3\ CaCl_2\ nH_2O + 2NO_2^- \quad (1)$$

Based on both effects of removing chloride ions and releasing nitrite ions, it is expected to effectively suppress the reinforcing bar corrosion.

3. Long-term exposure test

3.1. Preparation of specimen and exposure condition

Fig. 3 shows the dimensions of the large-size concrete specimen used in the long-term exposure test, in which the thickness of cover concrete is 25 mm to simulate a concrete slab. The mix proportion of the concrete is shown in Table 1; water–cement ratio 63.5% and the amount of chloride ions 4 kg/m^3. Half a year after casting the specimen, we repaired the central part, as shown in Fig. 3, by chipping off the original cover concrete until half of the main bar appeared, and by the restoring to the original cross-section with the repair mortar containing the salt adsorbent. After repairing, the outer half of surfaces of main bars were covered with the repair mortar. However, distribution bars were still totally buried in the original chloride containing concrete because these bars were situated deeper than the main bars. We selected seashore in Okinawa Islands as the exposure test site because the climate is hot and humid enough to accelerate the corrosion of reinforcing bars.

3.2. Investigation of the corrosion of reinforcing bars

To investigate the state of the corrosion of reinforcing bars after seven years exposure, we measured the half-cell potential by means of a reference electrode and high impedance potentiometer. With regard to the half-cell

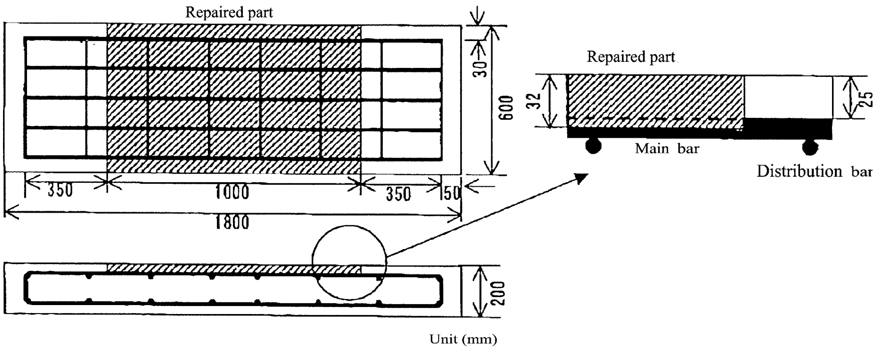

Fig. 3. Reinforcing bar arrangement and repaired part.

Table 1
Mix proportion of concrete

Maximum (coarse aggregate) size (mm)	Slump (cm)	Air content (%)	Water–cement ratio (%)	Quantity of material per unit volume of concrete (kg/m^3)			
				Cement	Water	Fine aggregate	Coarse aggregate
25	21.0	4.0	63.5	271	172	876	961

Cement: Ordinary portland cement; Fine aggregate: Sand; Coarse aggregate: Gravel; Chemical admixture: Air-entraining and water-reducing admixture.

potential correction procedure, according to the method we proposed [4], we corrected the potential, taking into consideration the water content and carbonation depth. The corrected half-cell potential around the edge of specimens was about −250 mV at the repaired part and about −400 mV at the unrepaired part, as shown in Fig. 4. Clear differences in the corrected half-cell potential between the repaired and unrepaired parts were found. Table 2 shows the estimation of the degree of corrosion from the corrected half-cell potential. Based on this table, it was judged that the reinforcing bars in repaired parts were in the state of the degree I or no corrosion. The corrected half-cell potential for reinforcing bars in repaired parts remained unchanged during the test period. It is found that the effect of the corrosion inhibitor had been maintained sufficiently for seven years. The corrected half-cell potential for reinforcing bars in unrepaired parts, which was about −400 mV, indicated that reinforcing bars in the parts were in the state of the degree III.

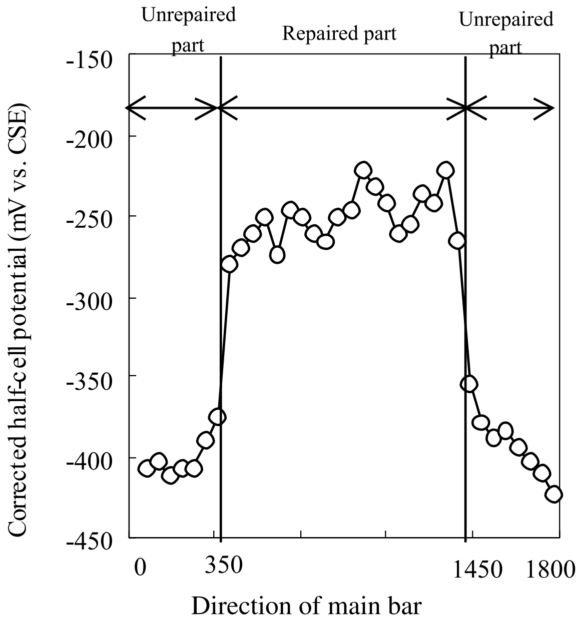

Fig. 4. Example of corrected half-cell potential along the main bar.

In the next step, to confirm the degree of the corrosion of reinforcing bars mentioned above, we chipped off the cover concrete in the areas including both the repaired and unrepaired parts, and then visually observed the state of the corrosion of reinforcing bar.

Fig. 5 schematically shows the states of the corrosion of reinforcing bars. No corrosion feature was on the main bars and ditribution bars in the repaired parts which had been judged as no corrosion by the corrected half-cell potentials. This means that the corrosion inhibitor was sufficiently effective even on the distribution bars in the repaired parts even after seven years exposure test in a saline environment. Both corrosion inhibitor and distribution bars of the unrepaired parts were under a state of slightly lifted rust on their surfaces. Thus, the states of corrosion of reinforcing bars were in

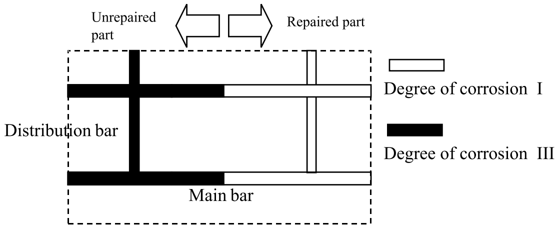

Fig. 5. Schematic drawing of the condition of reinforcing bar corrosion.

Table 2
Relationship between the corrected half-cell potential and the degree of reinforcing bar corrosion

Corrected half-cell potential	Degree of reinforcing bar corrosion	
$E > -250$ mV	I	No corrosion
-250 mV $> E > -350$ mV	II	Slight spot rust on the surface
-350 mV $> E > -450$ mV	III	Slightly lifted rust on the surface and rust adhered to the concrete
-450 mV $> E$	IV or over	Expansive rust and partial deficit, or more deteriorated

agreement with the results judged based on the corrected half-cell potential.

It is pointed out that a macro-cell is formed with the unrepaired part as the anode and the repaired part as the cathode, which accelerates the corrosion at the joint part. As far as the states of corrosion of reinforcing bars are concerned, however, repairing with the corrosion inhibitor of salt adsorbent also minimizes the possibility of macro-cell corrosion.

3.3. Corrosion inhibiting effect of the salt adsorbent

In order to discuss the effectiveness of the corrosion inhibitor, the profiles of chloride ions across the interface between repaired and unrepaired parts were obtained by measuring both ions content at various depths from surfaces.

Firstly, Fig. 6 shows the profiles of chloride ion. The thickness of repairing parts is 30 mm, and the inner parts deeper than 30 mm is original concrete. The depth of the center of main bars and that of the distribution bars are 30 and 40 mm, respectively.

In the original concrete, the total chloride ions content in deep parts is 3.7 kg/m^3, of which the content of soluble chloride ions was 1.2 kg/m^3 or about 30% of the total chloride ions content. During the exposure tests for seven years, chloride ions diffused into the repaired parts. Thus, the chloride ion content gradually decreased toward the interface. In the repaired parts, a large amount of chloride ions are found to penetrate through the interface. At parts in contact with the main bars, 2 kg/m^3 of total chloride ions, of which 0.2 kg/m^3 was soluble, were detected. When these ions had migrated into the repaired parts by diffusion, they must have been soluble. The ratio of the amount of soluble chloride ions to that of the total chloride ions indicates that about 90% of chloride ions were adsorbed and fixed. Chloride ions of about 1 kg/m^3 were detected in the repaired parts near the surface. A part of the chloride ions may have come from the outside. Soluble chloride ions were not detected near the surface. This shows that the penetrated salt was caught by the salt adsorbent.

Secondly, Fig. 7 shows the profiles of nitrite ion and soluble chloride ion. At about 20 mm from the interface toward the original concrete, as much as about 1 kg/m^3 of both nitrite and soluble chloride ions were detected. From Fig. 7, nitrite ions are found to penetrate up to about 50 mm away from the interface, at which chloride ions started to decrease. Many researches on the corrosion inhibiting effect of nitrite ion have been conducted by the use of the mole ratio of nitrite ion to chloride ion as an index. High corrosion inhibiting effect was obtained at the mole ratio of higher than 0.6 [5], and greater than 1 [6]. Although the relation between the mole ratio of nitrite to chloride ions and corrosion inhibiting effect depends on the quality of concrete, it is considered that rust can be prevented when the mole ratio is 0.6–1. Fig. 8 shows the mole ratio of nitrite ion to chloride ion at different depths. The mole ratio 1 and 0.6 were attained at 10 and 20 mm from the interface, respectively. Parts up to the position of distribution bar were in a sufficiently high corrosion inhibiting environment. As described above, it is found that the distribution bar, which was in a corrosive environment at the initial stage, has been varied at a sufficiently high-level of corrosion inhibiting environment during the exposure

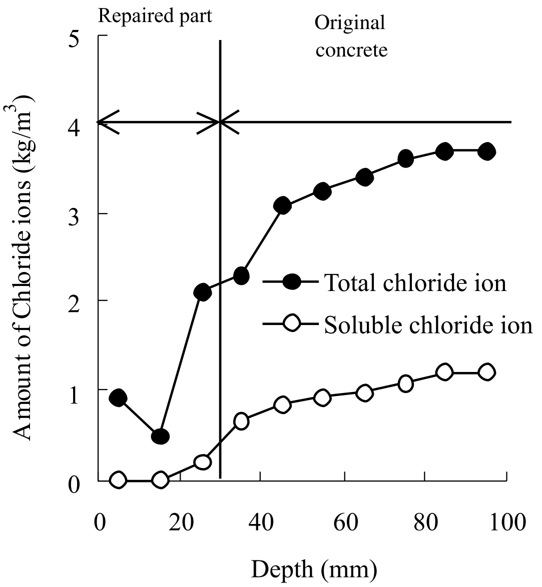

Fig. 6. Profile of chloride ion across the interface.

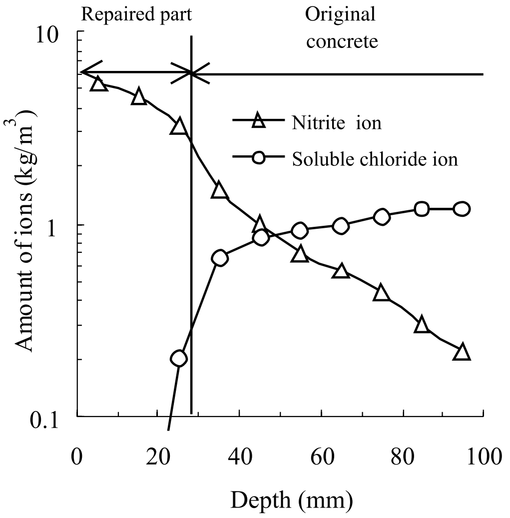

Fig. 7. Profile of soluble chloride ion and nitrite ion across the interface.

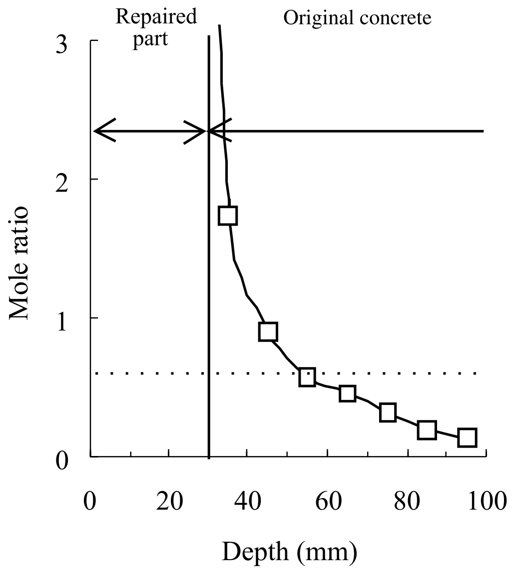

Fig. 8. Profile of Mole ratio (nitrite ion/soluble chloride ion) across the interface.

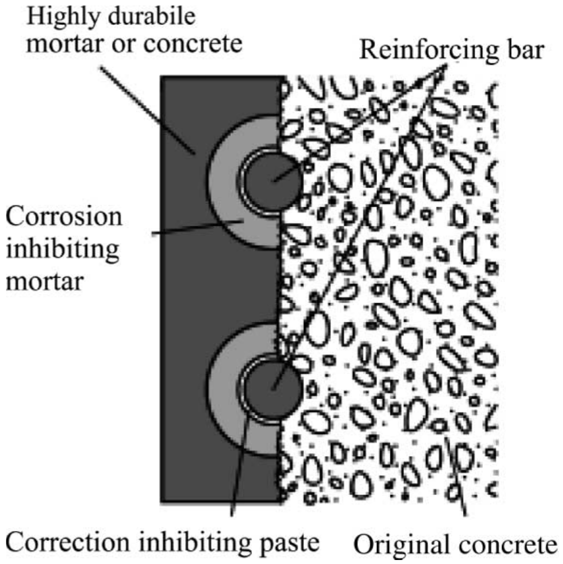

Fig. 9. Concept of SSI method.

test for seven years, as the environment of the concrete structure has been improved by the decrease in amount of chloride ions and the penetration of nitrite ions.

4. Suppression of corrosion of reinforcing bars and repair work

4.1. Repairing materials for corrosion of reinforcing bars

Based on the results obtained above, two repairing materials were prepared. One was a paste (referred to as "corrosion inhibiting paste") which was applied directly on the surface of reinforcing bars. The other was a mortar (referred to as "corrosion inhibiting mortar") which was applied to overlay of the layers around reinforcing bars. Both materials contained the salt adsorbent. The ratio of salt adsorbent to cement by weight was maintained at 0.2. A type of emulsion was added to both repairing materials to improve their workability. Measurements of compressive strength and other properties carried out according to the JIS standard procedures showed that the corrosion inhibiting paste and mortar were appropriate as repairing materials.

The application method of these materials was developed as the suppressing salt injury method (SSI method shown in Fig. 9). The application procedure consists of the following steps. At first, the cover concrete is chipped off until the reinforcing bars were exposed, and then the rust on the surfaces of the reinforcing bars was removed sufficiently. In the next step, the corrosion inhibiting paste is plastered on the surfaces of reinforcing bars with a thickness of about 1 mm, and then the corrosion inhibiting mortar is mounted to cover the paste layers with the thickness of 15–20 mm. In the final step, highly durable mortar or concrete was cast to finish the surface. This method not only replaces less durable concrete with highly durable mortar or concrete, but also suppresses the corrosion of reinforcing bars by the reduction of chloride ions in the backside of reinforcing bars and the addition of nitrite ions.

4.2. Trial of repair works in actual concrete structures

For conducting repair works, two concrete structures of the railway were selected; one a viaduct pier which is several kilometers away from the seashore, the other a concrete abutment of a railway station platform which is located in a cold weather district.

4.2.1. Repair work in a viaduct pier

The structure could be affected by the penetration of ground water containing sea water. To survey the deterioration of the structure, the half-cell potential measurement was conducted from the ground level up to a height of 750 mm in which area the deteriorated portion was included (Fig. 10).

The corrected half-cell potential values are shown in Fig. 11. The corrected half-cell potential was less noble than −250 mV from ground up to 400 mm height showing that the reinforcing bar is corroded, and that the corrected half-cell potential was nobler than −250 mV above a height of 400 mm showing the reinforcing bar is not corroded.

After chipping off the cover concrete and removing rust from the reinforcing bar, the SSI method was

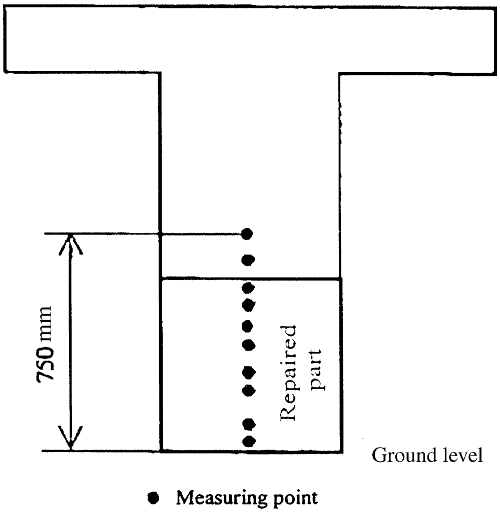

Fig. 10. Measuring points in viaduct pier.

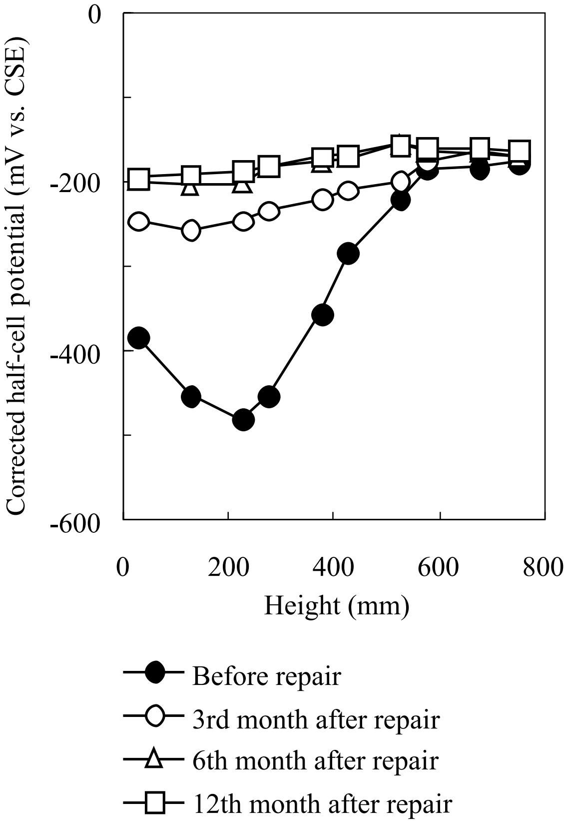

Fig. 11. Variations of the corrected half-cell potential.

applied. The repair process described in 4.1 followed, and high durable mortar was adopted in the finishing step. After repairing, the corrected half-cell potential at the repaired part was investigated to confirm the effect of the SSI method. Since the data immediately after the repair work scattered widely during the 1st month presumably because chloride ions and nitrite ions were in the diffusing process due to anion exchange, these data were omitted in the following discussion. Therefore, the data obtained only in the 3rd month or later were used. The variations of the corrected half-cell potentials are shown in Fig. 11.

In the 3rd month, the corrected half-cell potential became nobler than those before the repair work. In the 6th month, they shifted further to nobler side beyond −250 mV. In the 12th month, the corrected half-cell potential remained the level observed in the 6th month showing that the high corrosion inhibiting effect was maintained.

4.2.2. *Repair work in a platform abutment*

The structure could be affected by the leakage containing salt from deicing chemical (calcium chloride). To survey the deterioration of the structure, measurement of the half-cell potential was performed at nine points on the concrete surface (Fig. 12). The corrected half-cell potential values are shown in Fig. 12. The corrected half-cell potential was −310 to −340 mV at the inside point No. 1 and No. 2, −350 to −390 mV at the points No. 3 to No. 8, and −420 to −430 mV at the point No. 9 at the end of the abutment.

Based on the results mentioned above, it was found that the reinforcing bars were more corroded at the end of the abutment than at other positions. It was considered that the calcium chloride spread on the platform had penetrated inside from the end of the abutment to supply chloride ions to the concrete.

After chipping off the cover concrete and removing rust out of the reinforcing bar, the SSI method was applied. The variations of the corrected half-cell potential are shown in Fig. 13. In the 5th month, the corrected half-cell potential became −200 to −300 mV nobler than those before the repair work. In the 17th and 29th month, they shifted further to nobler side

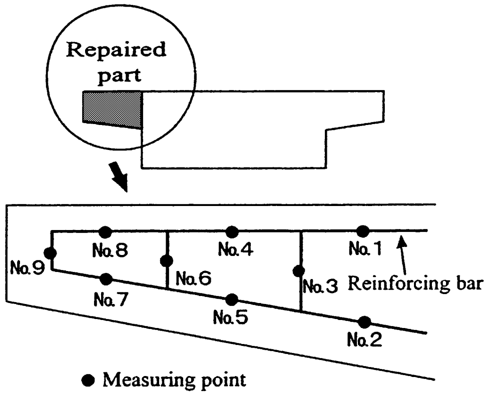

Fig. 12. Measuring points in platform abutment.

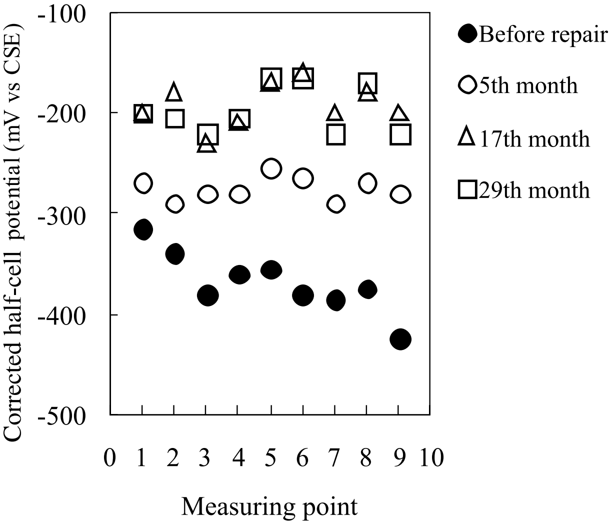

Fig. 13. Variations of the corrected half-cell potential.

beyond −250 mV, showing that the high corrosion inhibiting effect was maintained.

5. Conclusion

We synthesized a salt adsorbent which could release nitrite ions we used as a chloride-induced corrosion inhibitor. The effectiveness of the corrosion inhibitor was confirmed by the exposure tests and the repair works applied to actual concrete structures. The following results were obtained.

Firstly, to confirm the long-term corrosion inhibiting effect of the salt adsorbent developed to suppress the corrosion of reinforcing bars due to chloride ions, we prepared large-size specimens to simulate a slab, partly repaired them by mortars containing the adsorbent, and then exposed them to a high-temperature and humidity marine environment for seven years. It is clarified that the effectiveness of corrosion inhibitor has been maintained for a long time.

Secondly, to propose the repair procedure for inhibiting the corrosion of reinforcing bars, we developed the Suppressing Salt Injury method, named SSI method, using cement-based corrosion inhibiting materials which contain the newly developed adsorbent.

The method was applied to actual concrete railway structures. The structures which were repaired by the SSI method have been maintained at a sound state.

Acknowledgements

The authors wish to extend sinsere thanks to the Maintenance Division of the Highway Public Corporation Research Institute for their joint research of the repair system, and to the Maintenance Divisions of West Japan Railway Company for permitting of trial repair works to actual concrete structures. Special thanks are also given to Prof. M. Kawamura at Kanazawa University for giving us the opportunity to make this paper and Dr. K. Iwafuchi at the Railway Technical Research Institute for his assistance to complete this paper.

References

[1] Allen RTL, Edwards SC, Shaw JDN. The repair of concrete structures. Second ed. London: Chapman & Hall; 1993.

[2] Browne RD. Mechanisms of Corrosion of Steel in Concrete in Relation to Design, Inspection and Repair of Offshore and Coastal Structure, ACI SP-65, 1980.

[3] Kawamura M, Tanikawa S, Koto H. Pore solution composition and electrochemical behavior of steel bars in mortars with $Ca(NO_2)_2$ and $NaNO_2$. Concr Res Technol 1997;8(1):75–84 (in Japanese).

[4] Tatematsu H, Sasaki T. Studies on diagnosis and repair for reinforcing bar corrosion by salt injury. Trans Jpn Concr Inst 2000;22:211–20.

[5] Rosenberg AM et al. The inhibition of chloride-induced corrosion in reinforced concrete by calcium nitrite. American Society for Testing and Materials; 1980.

[6] Hori T, Yamasaki S, Masuda Y. A study on the corrosion inhibiting effect of mortar with high nitrite content. Concr Res Technol 1994;5(1):89–98 (in Japanese).