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CHLORIDE SHIELDING PERFORMANCE AND DURABILITY OF POLYMER-MODIFIED MORTAR LININGS FOR USE IN REINFORCED CONCRETE STRUCTURES EXPOSED TO MARINE ENVIRONMENTS

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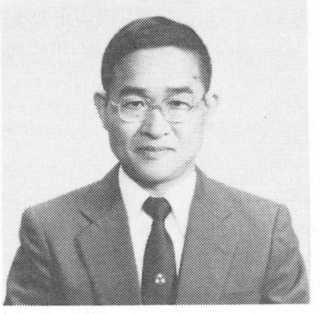
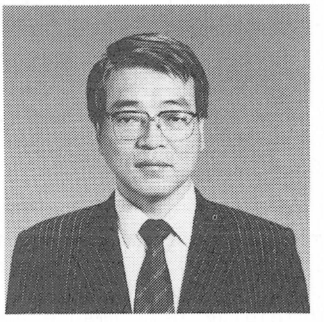

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SYNOPSIS

Reinforced concrete beam specimens with the polymer-modified mortar linings using a mixture of acrylic and epoxy emulsions are prepared, and exposed to a severe marine corrosion environment, where the beam specimens are continuously subjected to seawater splashes, for 5 years. The chloride shielding performance and durability of the polymer-modified mortar linings are examined through 5-year exposure by chemical analysis and EPMA area analysis. It is concluded from the test results that the polymer-modified mortar linings possess an excellent chloride shielding performance and durability because of the effective three-layer lamination of the polymer-modified mortar.

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1. INTRODUCTION

Polymer-modified mortars have widely been used as repair materials for reinforced concrete structures with chloride-induced corrosion or as corrosion protection linings for the reinforced concrete structures newly constructed in marine environments. However, the chloride shielding performance of the polymer-modified mortars has not always been made clear till now. In this paper, reinforced concrete beam specimens with polymer-modified mortar linings are exposed to a severe marine corrosion environment, where the reinforced concrete beam specimens are continuously subjected to seawater splashes for 5 years [1],[2]. It is concluded from the test results that the polymer-modified mortar linings possess an excellent chloride shielding performance and durability because of the effective three-layer lamination system of the polymer-modified mortar.

2. TESTING PROCEDURES

Two types of reinforced concrete beam specimens with and without polymer-modified mortar linings were exposed to a marine corrosion environment, where the reinforced concrete beam specimens were continuously subjected to seawater splashes for 5 years. During the exposure of the specimens, the chloride shielding performance and durability of the polymer-modified mortar linings have been examined by various tests and chemical analyses.

2.1 Materials

(1) Polymer-modified mortar for linings

Polymer-modified mortar using the materials shown in Table 1 was prepared with mix proportions of Main Materials : Mixture A : Mixture B = 79 : 17 : 4 (by weight) by using an electric stirrer for 4 to 5 minutes. The water-cement (ordinary portland cement plus blast furnace slag) ratio of the polymer-modified mortar with the mix proportions was 24 %. Table 2 gives the properties of Mixture A as a polymer dispersion.

Table 1 Materials for Polymer-Modified Mortar.

Main Material		Mixture A	
Material	Mix Proportion(%)	Material	Mix Proportion(%)
Cement	25	Aclyric Resin(48*)	86
Blast Furnace Slag	25	Epoxy Resin(67.5*)	14
		Mixture B	
Silica Powder	20		
Silica Sand	30	Material	Mix Proportion(%)
Reinforcement		Polyamide Resin(50*)	40
Glass Fibers : 11 μm x 6 mm		Water	60

Note, *:Total solids.

Table 2 Properties of Mixture A as Polymer Dispersion.

Specific Gravity (20℃)	pH (20℃)	Viscosity (20℃, cP)
1.092	10.3	460

(2) Concrete for reinforced concrete beam specimens

Materials for concrete were ordinary portland cement, Ohigawa river sand (F.M. 3.17, specific gravity 2.64 and water absorption 0.15 %) and crushed hard sandstone (maximum size 15 mm, specific gravity 2.70 and water absorption 0.47 %). The concrete was mixed with the following mix proportions : water-cement ratio 60 %, sand-aggregate ratio 47 % and unit cement content 327 kg/m^3, and its slump was adjusted to be 8 cm.

2.2 Preparation of Specimens

(1) Preparation of reinforced concrete beam specimens with and without linings

Reinforced concrete beam specimens 10 X 10 X 120 cm using two deformed bars (nominal diameter 10 mm and length 110 cm) were molded with cover thicknesses of 2 and 3 cm, and subjected to a 21-day spray cure outdoors. After curing, the specimens were lined with polymer-modified mortars to make the lined reinforced concrete beam specimens. Except the cast surface of the specimens, their five surfaces were treated with wire brushes, and lined with the polymer-modified mortar to be about 10 mm in thickness by a three-layer lamination system. Namely, the middle layer of the linings was applied at 18 hours after the applications of the under layer, and the top layer was done at 24 hours after the application of the middle layer.

(2) Fixation of reinforced concrete beam specimens under flexural loading

Polymer-modified mortar lined and unlined reinforced concrete beam specimens were fixed and exposed in parts under three-point flexural loading as shown in Fig. 1 at a marine exposure site. In the fixation of the specimens, the unlined specimens were loaded till the flexural crack width at a center of the span had indicated 0.2 to 0.3 mm on the tensile zone, and the lined specimens were done with the introduction of cracks under the same load as that for the unlined specimens. The plural cracks with widths of 0.2 to 0.3 mm occurred on the unlined specimens, but only one or two cracks did on the lined specimens.

2.3 Marine Exposure Test

Polymer-modified mortar lined and unlined reinforced concrete beam specimens were exposed at a marine exposure site in the east seaside of the Izu Peninsula, Ito, Shizuoka Prefecture, Japan. As seen in Photo 1, the specimens were installed to be parallel to wave direction on the racks at about 50 cm over the highest sea level. The exposure site was under an extremely severe

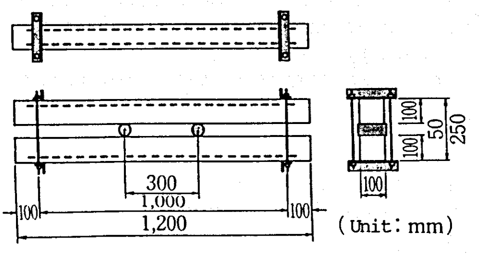


Fig.1 Exposed Reinforced Concrete Beam Specimens under Three-Point Flexural Loading.

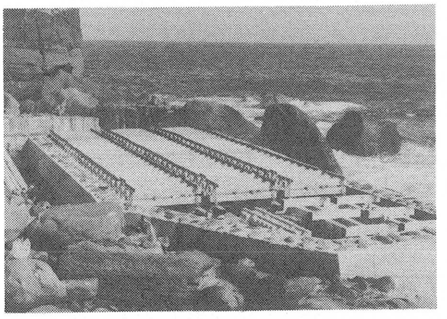


Photo.1 Exposure Site.

corrosion environment which was always subjected to seawater lashes at the flood tide and seawater splashes at the ebb tide. Therefore, it is considered that the environment of the exposure site comes under "Environment A" as prescribed in JCI-SC7 (Classification of Environments of Exposure Sites for Concrete Specimens).

2.4 Testing Procedures

(1) Observation of cracks and other deterioration of reinforced concrete beam specimens

The cracks and other deterioration of reinforced concrete beam specimens were observed at the exposure site at exposure periods of 6 months, 1, 2, 3, 4 and 5 years. In addition, the specimens were removed from the exposure site to the laboratory at exposure periods of 1, 3 and 5 years, and tested for chloride penetration into concrete and the corrosion of rebars.

(2) Measurements of corroded area ratio and average depth of corrosion of rebars in reinforced concrete beam specimens

Reinforced concrete beam specimens after 1-, 3- and 5-year exposures were split, and the locations of corrosion of rebars were sketched. The corroded portions of the rebars were traced, their corroded area was measured by an image processing analyzer, and their corroded area ratio was calculated. The rebar length for the corroded area measurement was 110 cm.

According to the marine exposure test results of reinforced concrete beams[2], it is evident that there is a considerable difference between the average weight losses of the rebars with the same corroded area ratio, and the rebars under a certain condition have any cross-section reduction. It is concluded from the test results to adopt the average depth of corrosion (i.e., average weight loss/corroded area) to quantitatively evaluate the corrosion of the rebars. As this value is small, the corrosion is limited to almost the surface layers of the rebars.

The average weight loss of rebars in reinforced concrete beam specimens was determined according to JCI-SC1 (Method of Evaluation for Corrosion of Reinforcing Steel in Concrete) as follows : the rebars with a length of about 15 cm, taken out from the specimens were immersed in 10 % diammonium hydrogen citrate solution for 2 days, the corrosion products on the surfaces of the rebars were brushed off, and their average weight loss was calculated by using the weights of the rebars before and after corrosions.

(3) Analysis of chloride in reinforced concrete beam specimens

Samples for chloride analysis were taken out at intervals of 10 mm of the surfaces of reinforced concrete beam specimens by using an electric drill with a diameter of 30 mm for concrete. The total chloride content of the samples was determined by the potentiometric titration prescribed in JCI Standard (Method of Analysis for Chloride Ions in Hardened Concrete).

(4) EPMA area analysis of chlorine and carbon in reinforced concrete beam specimens

To check chlorine distribution through the full cross-sections of reinforced concrete beam specimens, samples with a thickness of about 10 mm were cut out from the portion of the specimens as shown in Fig.2. The surfaces of the samples were ground, deposited with carbon, and subjected to EPMA area analysis.

To check chlorine and carbon distributions through the lining layers on reinforced concrete beam specimens, samples with a thickness of about 10 mm were cut out from the portion of the specimens as seen in Fig.8. EPMA area analysis of the surfaces of the samples was done in the same manner as stated above.

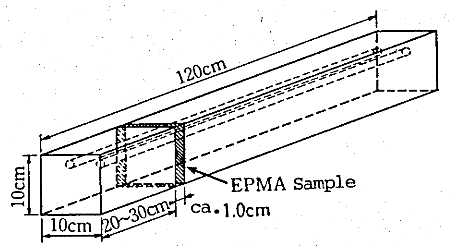


Fig.2 Portion of Sample for EPMA Area Analysis.

(5) Adhesion test of linings on reinforced concrete beam specimens

Adhesion between the linings and concrete of polymer-modified mortar lined reinforced concrete beam specimens was tested by a pull-out adhesion testing machine. For comparison, the adhesion test of unlined reinforced concrete beam specimens was made by the same method.

(6) Oxygen diffusion test of reinforced concrete beam specimens

Samples 10 X 10 cm with a thickness of about 20 mm, including the lining layers and concrete, cut out from polymer-modified mortar lined reinforced concrete beam specimens, and tested for oxygen diffusion according to JCI-DD5 (Method of Test for Oxygen Diffusion Coefficient of Concrete).

3. TEST RESULTS AND DISCUSSION

3.1 Corroded Area and Average Depth of Corrosion of Rebars

Fig.3 shows the corroded area ratio and average depth of corrosion of the rebars taken out from polymer-modified mortar lined and unlined reinforced concrete beams with flexural cracks after 5-year exposure. The corroded area ratio of the rebars in the polymer-modified mortar lined reinforced concrete

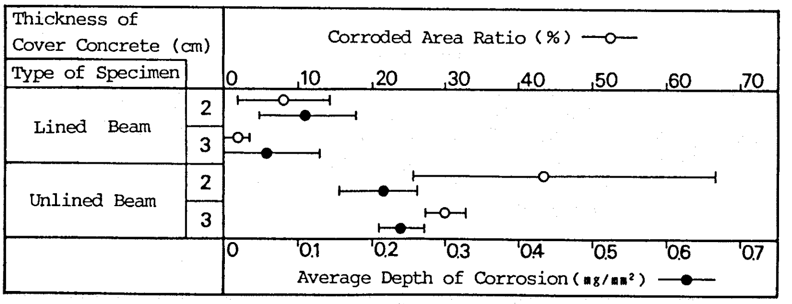


Fig.3 Corroded Area Ratio and Average Depth of Corrosion of Rebars in Reinforced Concrete Beams after 5-Year Exposure.

beam is markedly reduced at the respective cover thicknesses as compared to that of the rebars in the unlined reinforced concrete beams. On the other hand, the average depth of corrosion of the rebars in the polymer-modified mortar lined reinforced concrete beams is about a half of that of the rebars in the unlined reinforced concrete beams. This means the excellent corrosion-inhibiting effect of the polymer-modified mortar on the rebars. The rebar corrosion of the polymer-modified mortar lined reinforced concrete beams causes in the cracks introduced before exposure, and is not found out except the cracks at any cover thicknesses. In the formation of anticorrosive or corrosion protection layers such as linings on the concrete surfaces, this fact suggests that it is most important not to make any defects in the anticorrosive or corrosion protection layers.

Fig.4 represents the relation between the exposure period and corroded area ratio of the rebars taken out from the exposed polymer-modified mortar lined and unlined reinforced concrete beams with a cover thickness of 2 cm. The corroded area ratio of the rebars in the unlined reinforced concrete beams increases with additional exposure period, and sometimes attains to 60 % or more at an exposure period of 5 years. By contrast, the progress of the corrosion of the rebars in the polymer-modified mortar lined reinforced concrete beams is considerably slow at exposure periods of 1 year or more.

Accordingly, it is evident from Figs.3 and 4 that the 5-year exposure of the polymer-modified mortar lined reinforced concrete beams under a severe marine corrosion environment such as splash zone causes only a slight increase in the corroded area ratio of the rebars in the beams.

3.2 Penetration of Chloride into Concrete

Fig.5 illustrates the chloride penetration behavior of polymer-modified mortar lined reinforced concrete beams after 1-year, 3-year and 5-year exposures. The chloride content of the polymer-modified mortar lined concrete portion in Fig.5 is the average chloride content at a full thickness of the lined concrete portion. An increase in the chloride content of the lined concrete portion with additional exposure period is recognized, but the chloride penetration into the concrete is found to be almost completely inhibited by the polymer-modified mortar linings. Fig.6 shows the comparison of the chloride penetration behavior of the polymer-modified mortar lined and unlined reinforced concrete beams after 5-year exposure. It is obvious from Fig.6 that the polymer-modified mortar linings have an excellent chloride shielding performance.

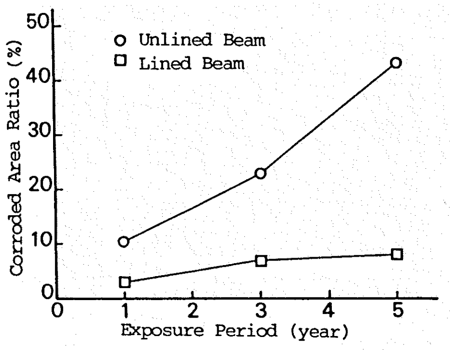


Fig.4 Relation between Exposure Period and Corroded Area Ratio of Rebars in Reinforced Concrete Beams with Cover Thickness of 2cm.

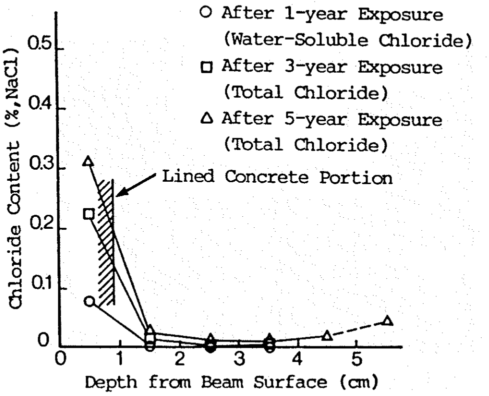


Fig.5 Chloride Penetration Behavior of Polymer-Modified Mortar Lined Reinforced Concrete Beams.

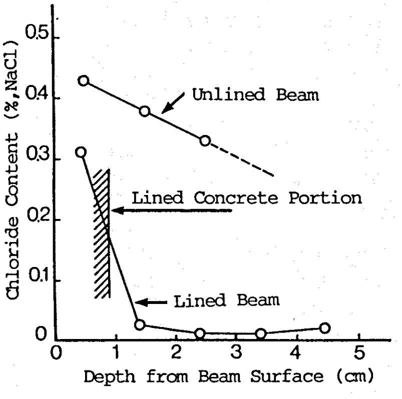


Fig.6 Comparison of Chloride Penetration Behavior of Polymer-Modified Mortar Lined and Unlined Reinforced Concrete Beams.

3.3 Chlorine and Carbon Distributions by EPMA Area Analysis

Chlorine determination by EPMA area analysis was conducted to observe chloride shielding performance through the full cross-sections of polymer-modified mortar lined and unlined reinforced concrete beams and to confirm the effectiveness of the polymer-modified mortar linings.

Photos 2 and 3 shows the chlorine distribution through the full cross-sections of unlined and polymer-modified mortar lined reinforced concrete beams respectively. White color parts in the photos indicate relatively high chlorine content, and darker color parts do lower chlorine content. A part with higher chlorine content on the lower portion of Photo 3 indicates the chloride penetration from the unlined cast surface of the concrete beam. In seen in this photo, the polymer-modified mortar linings effectively shield from the chloride penetration into the concrete.

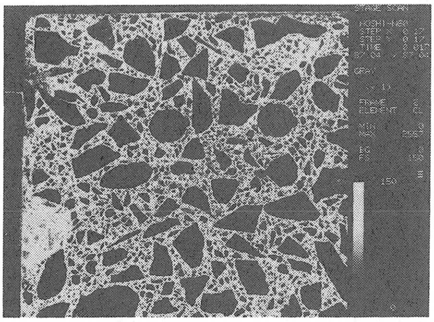


Photo.2 Chlorine Distribution of Unlined Reinforced Concrete Beam.

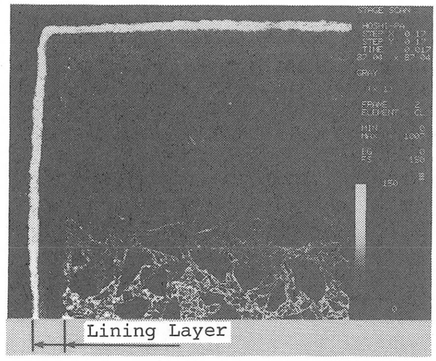


Photo.3 Chlorine Distribution of Polymer-Modified Mortar Lined Reinforced Concrete Beam.

Photo 4 indicates the chlorine distribution of the respective layers of a polymer-modified mortar lining in Fig.8. In this photo, the chlorine content is the highest in the top layer, gradually decreases from the middle layer to the under layer, and is zero (i.e., the complete background level) in the under layer, i.e., the interface between the lining layer and concrete. Figs.6 and 7 represent the chlorine contents determined by the chemical analysis of the portions shown in Photos 2 and 3, and Photo 4 respectively. The chlorine contents well correspond to the EPMA area analysis results.

The above chloride shielding performance of polymer-modified mortar linings closely relates with a three-layer lamination lining system for the polymer-modified mortar. Carbon determination by EPMA area analysis was performed to observe carbon distribution through the full cross-sections of the polymer-modified mortar linings and to examine polymer distribution through the three-layers of the linings. Because the main chemical compositions are carbon, oxygen, hydrogen and nitrogen, and the parts with a high carbon content correspond to ones with a high polymer content. Photo 5 gives the carbon distribution through three layers of the linings. Two white linear parts in this photo mean the presence of a large quantity of carbon. However, the carbonization of the linings may also cause an increase in the carbon content. The parts were observed by a polarization microscope to check their microstructures. Photo 6 shows two polarization microscope photographs of the linings. From this photo, the part indicated by each arrow is a linear structure under parallel nicols , and a noncrystalline structure under crossed nicols. In other words, this part is due to the formation of dense polymer films, which are found to effectively shield from chloride penetration. To form the dense polymer films in the linings, the middle layer was lined after the sufficient cure of the under layer, and the top layer was done after the sufficient cure of the middle layer. When the polymer-modified mortar is applied in such thin layers, the fine polymer particles in the polymer dispersions concentrate in their surfaces with water evaporation, and the dense polymer films are formed. Such dense polymer microstructures can be recognized by observing the cross-sections of the linings as shown in Photo 7.

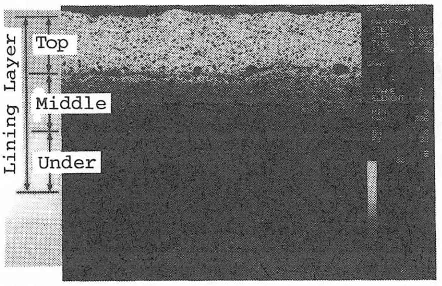


Photo.4 Chlorine Distribution of Polymer-Modified Mortar Lining Layers.

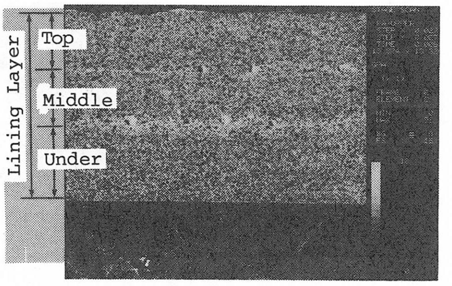
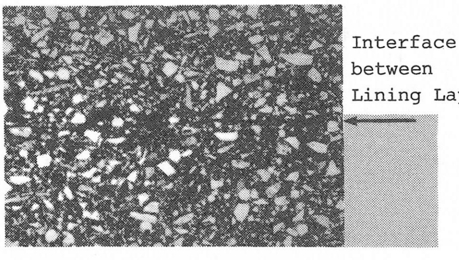
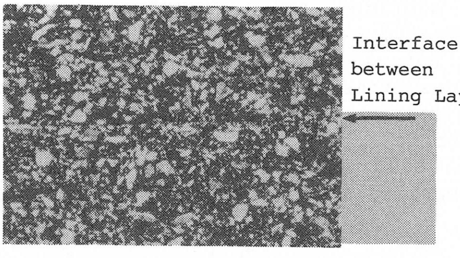


Photo.5 Carbon Distribution of Polymer-Modified Mortar Lining Layers.



Under Parallel Nicols



Under Crossed Nicols

Photo.6 Polarization Microscope Photographs of Polymer-Modified Mortar Linings (x40).

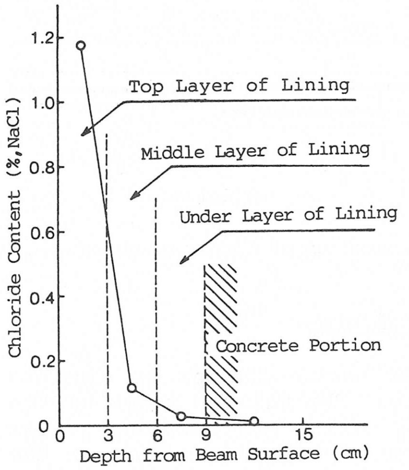


Fig.7 Chloride Shielding Peformance of Three-Layer Lamination System of Polymer-Modified Mortar after 5-year Exposure.

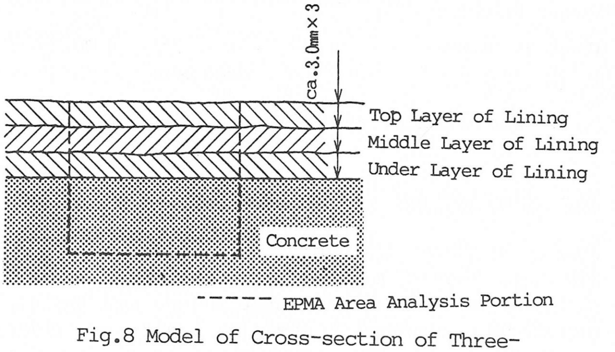


Fig.8 Model of Cross-section of Three-Layer Lamination System of Polymer-Modified Mortar.

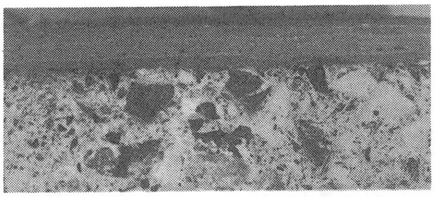


Photo.7 Cross-sections of Polymer-
Modified Mortar Lining Layers.

3.4 Cracks of Concrete and Corrosion of Rebars

Fig.9 illustrates the change of the cracks of reinforced concrete beams with additional exposure period and the locations of corrosion on the rebars taken out from polymer-modified mortar lined and unlined reinforced concrete beams after 5-year exposure. Gray parts in this figure indicate dot-like rust on the surfaces, and black parts do corrosion with reduced cross-sections. In the polymer-modified mortar lined reinforced concrete beams, some corrosion of the rebars is detected, but the patterns of the concrete cracks introduced before exposure hardly change at an exposure period of 5 years. By contrast, in the unlined reinforced concrete beams, longitudinal cracks occur on the concrete surfaces along rebar locations at an exposure period of 1 year, and the sealing of the concrete and the corrosion of the rebars are widely recognized at an exposure period of 5 years.

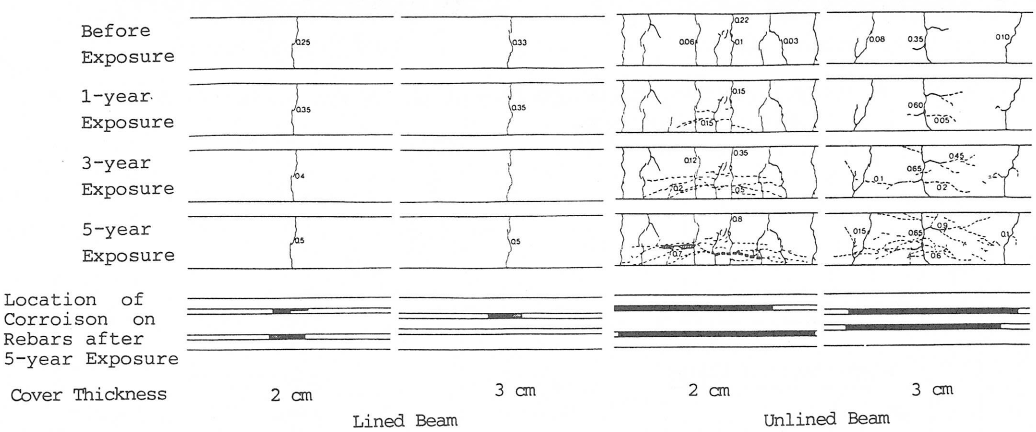


Fig.9 Cracks of Reinforced Concrete Beams and Loacation of Corrosion on Rebars.

3.5 Adhesion and Oxygen Diffusion Coefficient of Linings

Table 3 gives the adhesion of polymer-modified mortar linings to concrete through 5-year exposure to marine splash zone. The failure modes of the polymer-modified mortar linings are cohesive failure in the concrete at exposure period of 1 year or less, and almost mixed cohesive failure in the linings and concrete, sometimes, cohesive failure in the concrete at exposure periods of 3 years or more. Furthermore, the average adhesion increases with additional exposure period. As the adhesion of polymeric coatings as repair materials for concrete structures to the concrete generally is 10 to 20 kgf/cm^2, the adhesion between the linings and concrete under the severe marine

Table 3 Adhesion of Polymer-Modified Mortar Linings to Concrete through 5-year Exposure.

Exposure Period (year)	Adhesion (kgf/cm^2)	Average of Adhesion (kgf/cm^2)	Failure Mode
Before Exposure	24	27	Cohesive Failure in Concrete
	26		
	30		
1	28	30	Cohesive Failure in Concrete
	30		
	33		
3	38	34	Cohesive Failure in Lining
	28		Mixed Cohesive Failure in Lining and Concrete
	37		
5	50	50	Cohesive Failure in Concrete
	53		Mixed Cohesive Failure in Lining and Concrete
	48		

corrosion environment such as splash zone is found to be excellent as seen in Table 3.

On the other hand, the progress of the corrosion of rebars in concrete structures needs the active supply of oxygen after the failure of passive films on the rebars due to the progress of carbonation and chloride penetration near them. The degree of oxygen supply can be quantitatively expressed by the oxygen diffusion coefficient of the materials surrounding the rebars, generally concrete, concrete with linings in this paper. Although polymer-modified mortar linings are applied on reinforced concrete beams, it is evident from Figs.3 and 4 to corrode the rebars under the cracks which are formed in the linings, induced by concrete cracks. These figures also demonstrate that the corrosion rate of the rebars in the lined reinforced concrete beams is smaller than that of the rebars in the unlined reinforced concrete beams. When the anode of corrosion cell on the rebars in cracked portion and the cathode of the cell in the surrounding are formed, and the presence of the linings controls oxygen supply to the cathode, it is considered that the corrosion rate of the rebars is decreased. It is pointed out that the oxygen diffusion coefficient of the polymer-modified mortars is considerably smaller than that of ordinary concrete [3]. To confirm this fact in the present study, test pieces with a thickness of about 20 mm were taken out from the lined reinforced concrete beams after 5-year exposure, and tested for oxygen diffusion by a diffusion cell method [3]. As a result, the oxygen diffusion coefficient of the lined reinforced concrete beams is 0.2 to 0.4 X 10^{-4} cm^2/s, and that of the unlined reinforced concrete beams is 3 to 4 X 10^{-4} cm^2/s. Such data demonstrate that the oxygen diffusion behavior of the polymer-modified mortar linings contributes to the corrosion protection of the rebars in the reinforced concrete beams.

4. CONCLUSIONS

The corrosion protection effect of polymer-modified mortar linings on the reinforced concrete structures which are constructed in marine environments has hardly been clarified till now. In this paper, the excellent durability and chloride shielding performance of such linings are made clear. The chloride shielding mechanism of the linings is examined by using the results of EPMA area analysis, and it is confirmed that the three-layer lamination lining system plays an important role for chloride shielding.

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