Third International Conference on Sustainable Construction Materials and Technologies http://www.claisse.info/Proceedings.htm

Durability of Marine Concrete with Mineral Admixture and Marine Aquatic Organism Layer

Amry Dasar[1], Hidenori HAMADA[1], Yasutaka SAGAWA[1] and Takanori IKEDA[2]

[1]*Kyushu University, Japan*
[2]*Maeda Corporation, Japan*
[1]*West 2 Building, Room 1103, 744 Motooka, Nishi-Ku, Fukuoka, Japan, 819-0395*
[2]*1-39-16, Asahi-cho, Nerima-ku, Tokyo, Japan, 179-8914*
e-mail: *amrydasar@doc.kyushu-u.ac.jp, h-hamada@doc.kyushu-u.ac.jp, sagawa@doc.kyushu-u.ac.jp, and ikeda.t@jcity.maeda.co.jp*

ABSTRACT

The high chloride ion concentration along with the presence of oxygen and water leads to accelerated corrosion process. It is fact that, durability of marine concrete depends corrosion resistance of concrete. On the other hand, addition of mineral admixture and covered marine aquatic organism layer has a potential to reduce the risk of corrosion. A total of 6 samples were prepared which had been exposed in the marine environment for 13 years. During the initial several years, marine aquatic organism layer was formed. In order to investigate the effect of mineral admixture and marine aquatic organism layer against corrosion, experimental laboratory study was carried out to measure corrosion potential and micro-pore structures related to the rate of chloride ion diffusion. Results show that mineral admixture can reduce the risk of corrosion. Moreover, marine aquatic organism layer had a positive effect to prevent the chloride ingress into concrete.

Keywords: mineral admixture, marine aquatic organism, corrosion.

INTRODUCTION

One of the main cause of steel reinforced concrete degradation is by electro-chemical deterioration due to chloride ion. Reinforced steel embedded in concrete has passivity film, however, this layer would be damaged associated with increments of chloride ion content. In addition, the presence of water and oxygen could accelerate the corrosion process. In this experiment, during 13 years exposure in the marine environment, marine aquatic organisms were formed on the concrete surface. In order to investigate the effect of mineral admixture in improving resistance of concrete against corrosion and also effect of covered marine aquatic organism layer, experimental test, consisting of corrosion potential of steel, diffusion coefficient of chloride ingress, compressive strength, microstructure by Scanning Electron Microscope (SEM) and mercury intrusion porosimetry (MIP), were carried out.

METHODOLOGY

Sample Background. There are six samples taken from Shimizu Port of Shizuoka Prefecture, Japan. Physical properties of the material and mix proportions of the sample are shown in Table 1 and Table 2, respectively with water to binder ratio (W/B) of 40% and 55%. Reinforced concrete (RC) with single plain bar ϕ16 mm specimens with dimensions of 100 x 100 x 400 mm and cover depth 50 mm were prepared for the exposure test. Cement paste cubic with size of 150 mm was also exposed for microstructure analysis by SEM.

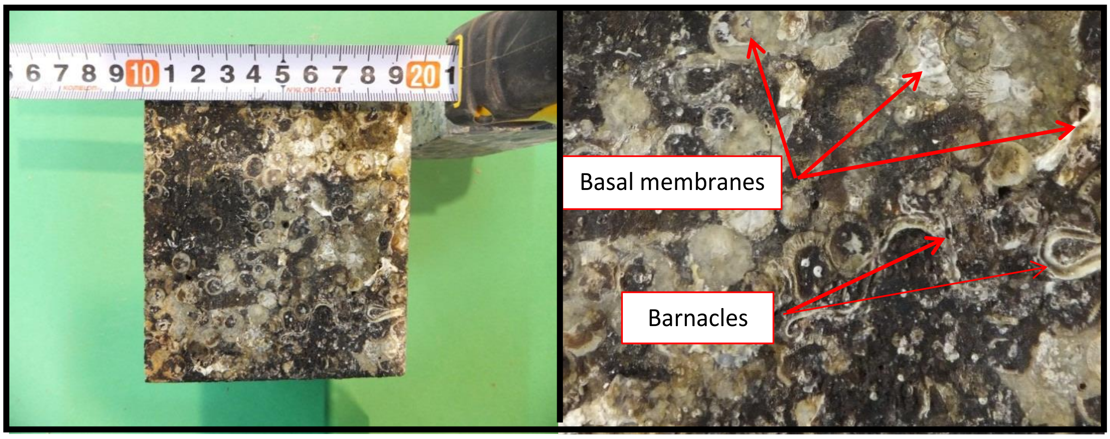
Table 1. Physical Properties

Material	Type	Physical Properties		F.M.
		Density (g/cm³)	SS (cm²/g)	
Cement	OPC	3.15	3396	-
Blast Furnace Slag	BFS 4000	2.87	4270	-
Fly Ash	Class II (JIS A 6201)	2.20	3380	-
Sand	River sand	2.58	-	2.77
Gravel	Crushed gravel	2.71	-	6.97

Table 2. Mix Proportion of Concrete

Name	W/B	Unit Weight (kg/m³)							
		W	Binder			Special Admixture*	Sand	Gravel	C.A
			C	BFS	FA				
A	0.55	176	320	-	-	-	793	986	0.8
B	0.55	176	176	144	-	-	765	986	0.8
C	0.55	176	220	-	96	-	748	986	0.8
D	0.40	170	420	-	-	-	748	986	1.05
E	0.40	145	316	-	-	47	847	986	-
F	0.40	145	221	-	95	47	821	986	-

*High-strength cement admixture which forms ettringite in cement matrix for high strength



Mix B for migration test (100 mm x 100 mm); Covered area 96.2 %

Photograph 1. Marine aquatic organism layer

The sample has been kept in marine environments for 13 years with tidal and submerged zone condition. During this period, marine aquatic organism was formed on the concrete surface as shown in Photograph 1, which acted as a barrier to the chloride ion penetration into concrete.

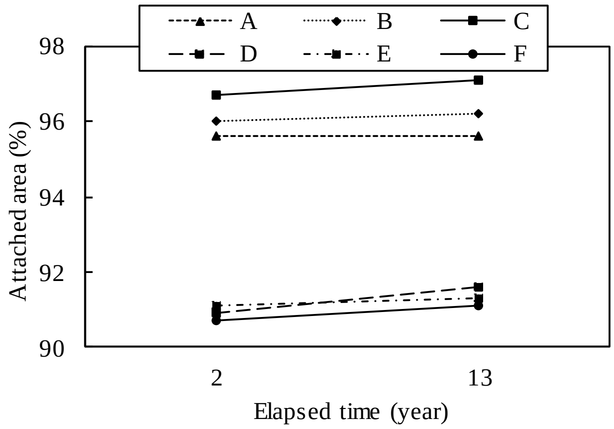


Figure 1. Percentage of area covered by marine aquatic organism

Previous research (Watanabe, 2002) shows marine aquatic organism attached on the concrete only after six months exposure. After two years exposure, more than 90% of the concrete surface was attached by marine aquatic organism shown in Figure 1. The covered area after 13 years was: 95.6% (Mix A), 96.2% (Mix B), 97.1% (Mix C), 91.6% (Mix D), 91.3% (Mix E) and 91.1% (Mix F).

Experimental Methods. Experimental laboratory test were performed:

Corrosion potential of the following steel bars inside concrete can be estimated using adaptable, and nondestructive measurements, an electrochemical technique known as half-cell potential test.

Polarization curve was measured in order to evaluate the condition of passivity film on the steel surface embedded in concrete. In the laboratory, polarization curve can be applied on the sample immersed in liquid solution. There are two procedures, firstly a sample with covered of marine aquatic organism was measured. Secondly, after marine aquatic organism was removed by using grinding machine, anodic and cathodic polarization curve was measured.

After non-destructive measurements, concrete was crushed and reinforced steel was taken out and areas of corrosion was observed and measured quantitatively as the corrosion area of reinforcement. Area of corrosion versus all surface areas is shown in the percentage.

Scanning electron microscope (SEM) is one of the highly precision equipment available for the microstructure observation and analysis of the sample material. The samples was cut into small pieces of 10 x 10 x 10 mm and mounted using epoxy resin. Then, sample surface was polished after epoxy reached hardened condition.

According to JSCE-G571-2010, the effective chloride diffusion coefficient was measured. The procedure was that the amount of negatively charged chloride ions migrating from cathodic cell toward anodic cell through concrete pore solution was measured under the steady chloride flow. There are two procedures employed in this experiment. Firstly, a sample with presence of marine aquatic organism on the concrete surface was set up and D_e was measured. Secondly, marine aquatic organism was removed by using grinding machine, then, D_e was measured.

For the measurement of apparent diffusion coefficient (D_a), a sample was cut to four layers from the surface of concrete, with 10 mm thick for each layer. Then chloride ion concentration of each layer was measured by the potentiometric titration method.

Pore size distribution was measured by 5-mm-thick samples cut from identically produced and cured cylinders. The fragments were dried in the vacuum desiccator for 2 days, previously dipped into the acetone about 15 min. Then pore size distribution of the samples was evaluated by MIP (Mercury Intrusion Porosimetry).

Sample was cut into cubic type of 40 mm. Then, the sample surface was polished until being flat. Then load applied into cubic sample until failure, and compressive strength was calculated.

RESULTS AND DISCUSSION

Half - cell Potential. Assessment on grades of corrosion risk for steel reinforcing bar due to half-cell potential is given in Table 3 according to ASTM C876-09. As we can see in Figure 2, for concrete with OPC, difference in W/B gave different effect. Sample A (0.55 W/B) shows the potential of -221.6 mV, and for the sample D (0.40 W/B) the potential is -102.6 mV. Potential value became lower as W/B increased. Furthermore, partial replacement of cement with mineral admixture gave positive effect to increase the potential value compared with OPC only. Partial replacement of cement with fly ash showed the best performance.

Table 3. Probability of corrosion (ASTM C876-09)

Half-cell Potential Reading (V, CSE)	Corrosion Activity
-200 < E	90% probability of no corrosion
-350 < E < -200	Uncertainty
E < -350	90% probability of corrosion

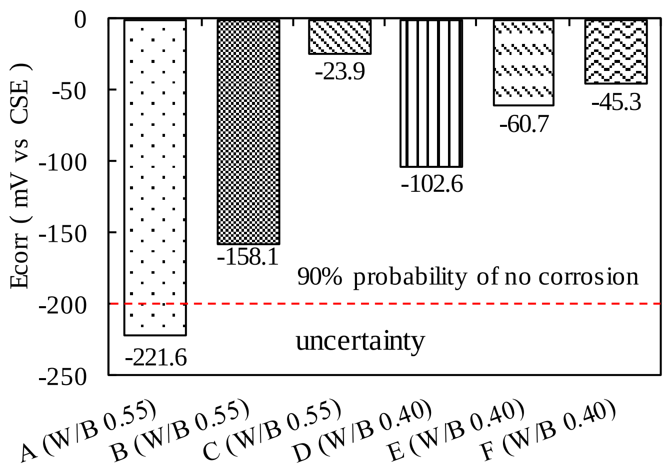


Figure 2. Potential cell

The results of polarization resistance is presented in Figure 3. Sample A with W/B of 0.55 showed lower polarization resistance, compared to the sample D with W/B 0.40. This figure shows that polarization resistance increase as W/B decrease. A partial replacement of cement achieved high of polarization resistance compared with OPC for the same W/B. Partial replacement of cement with mineral admixture shows more effective than OPC only. It can be suggested that partial replacement of cement with mineral admixture and the special admixture used for high strength concrete. The combination of fly ash and the special admixture showed best performance in the polarization resistance which gave the lowest corrosion rate.

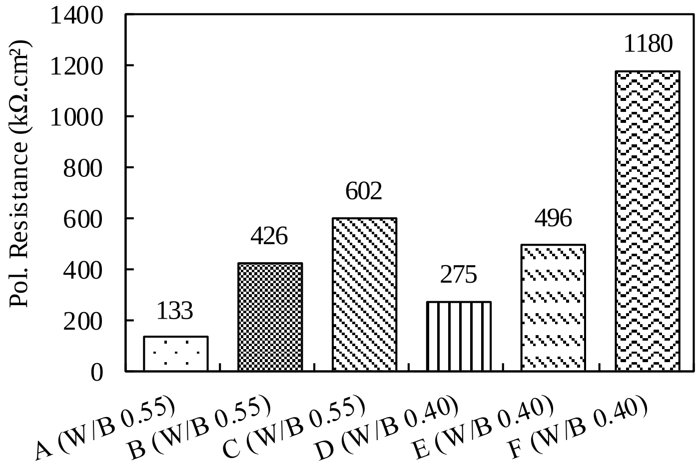


Figure 3. Polarization resistance

Figure 4 shows the result of corrosion current density I_{corr} which is inversely proportional to polarization resistance. When polarization resistance is low, I_{corr} value is high. Difference in W/B, partial replacement of cement with mineral admixture and usage of the special admixture, affected corrosion current of reinforced steel in concrete. Sample A with W/B of 0.55 showed high rate of corrosion, while sample D with W/B of 0.40 showed low rate of corrosion. This figure shows that corrosion current increase as a W/B increase. A combination of Fly Ash and the special admixture showed the best performance in corrosion current which means lowest corrosion rate.

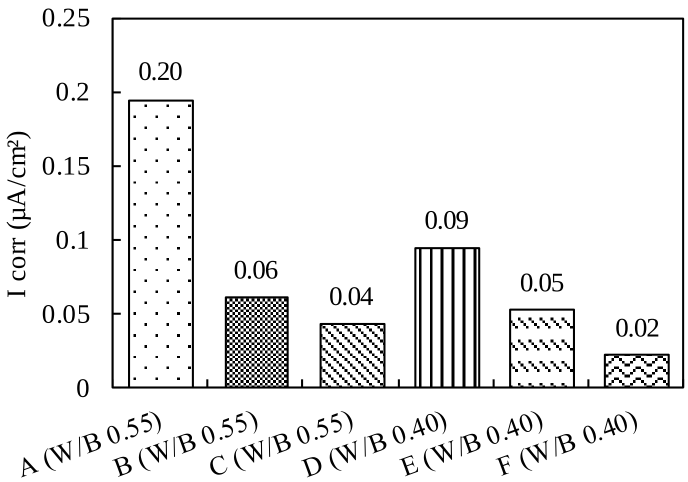


Figure 4. Corrosion current density

Polarization curve. According to Otsuki (1985), judgments standard of passivity grade (condition) of embedded steel bar was proposed by the polarization curve measured by the immersion method. Anodic polarization curve is shown in Figure 5. Sample A with W/B of 0.55 showed current density almost 10 μA/cm², which is categorized in the Grade 3 (certain degree of passivity exist), while sample D with W/B of 0.40 showed current density over 1 μA/cm² with categorize in the Grade 4 (certain degree of passivity exist, but not to qualified to grade 3). This figure shows that the current density increases as the W/B increases. Partial replacement of cement by fly ash and the special admixture showed effective decreasing in current density compared to the mineral admixture and OPC only. This is showed in sample F with current density almost 1 μA/cm² with categorize in Grade 4.

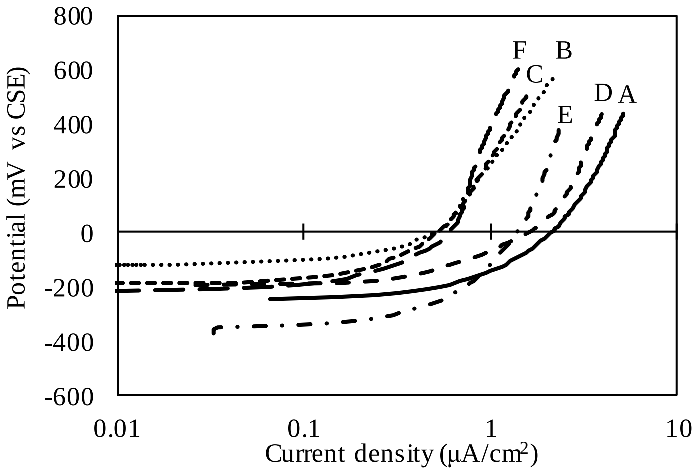


Figure 5. Anodic polarization curve

Cathodic polarization curve was used in order to know the grade levels of oxygen supplies into the concrete. The results shown in Figure 6 obtained from the cathodic polarization curve by the immersion method showed a similar trend with anodic polarization curve. It is clearly seen that the result in different between with cover and without cover of marine aquatic organism. Again, a partial replacement of cement by a combination of fly ash and the special admixture showed the best performance to prevent from the oxygen supplies.

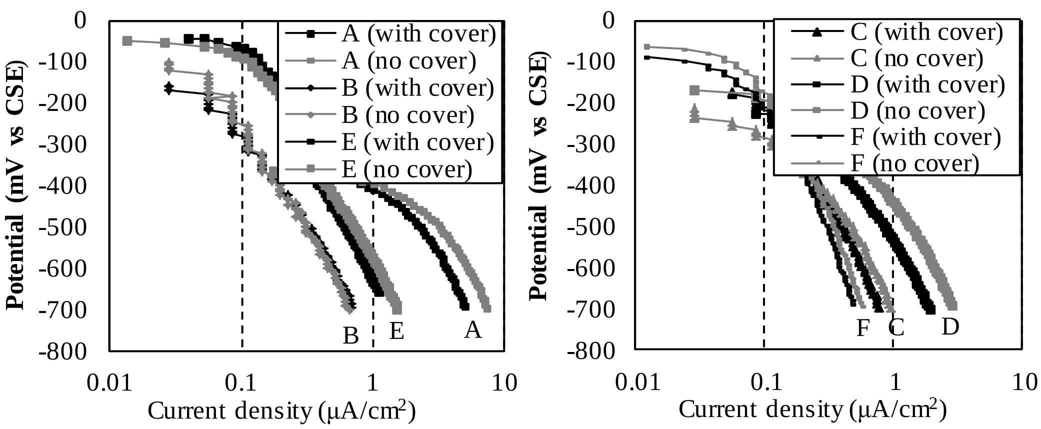
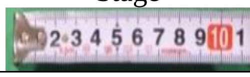


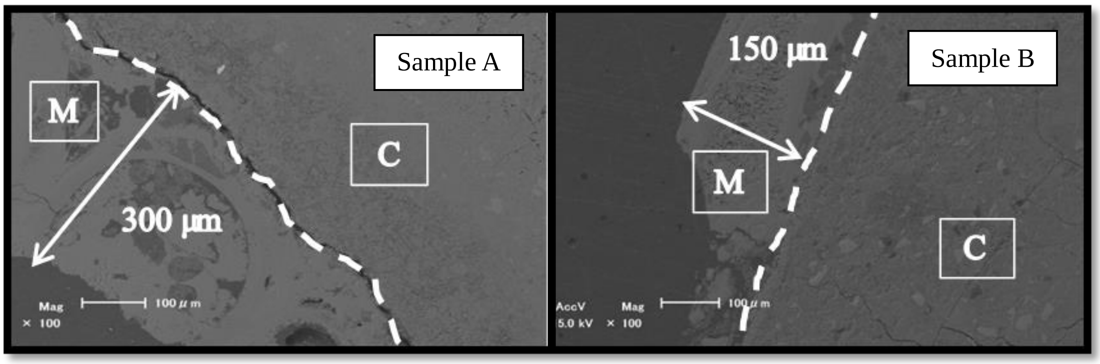
Figure 6. Cathodic polarization curve

Corrosion of Steel Bar. Corrosion condition and corroded area are shown in Table 4. Sample A of 0.55 W/B showed the corroded area about 17.87%, while sample D of 0.44 W/B showed no corrosion. It can be suggested that the risk of corrosion increased as increasing in W/B. The corrosion area on the steel surface was detected only on the steel reinforcement of sample A. Sample D included a high chloride concentration. However, steel corrosion didn't occur in the sample D. This result was considered that marine aquatic organism layer has potential which can prevent a diffusion of oxygen. On the other hand, positive effect also continued for the replacement of cement by some mineral admixtures. This is proved by all samples with partial replacement of cement, in the samples, no corroded area was found. Partial replacement of cement by a combination of fly ash and the special admixture showed the best performance to improve the passivity film and to reduce risk of corrosion.

Table 4. Corrosion condition and corroded area

Name	W/B	Type	Cover Thickness (cm)	Corroded Area (%)	Corrosion Stage 	Cl^- Concentration (kg/m³)
A	0.55	OPC	4	17.87		9.13
B	0.55	BFS	4	0		0.20
C	0.55	FA	4	0		0.16
D	0.40	OPC	4	0		8.22
E	0.40	EM	4	0		0.28
F	0.40	FA+EM	4	0		0.06

Scanning Electron Microscope (SEM). In concrete structures under marine environment especially in the tidal zone, marine aquatic organism layer adhere on the surface of concrete. Marine aquatic organism layer in the surface of concrete can be seen just like surface coating for concrete. Backscattered Electron Image from SEM is shown in Photograph 2. The average thickness of marine aquatic organism layer is about 200µm.



M – Marine aquatic organism layer; C – Cement paste

Photograph 2. Scanning electron microscope

Effective diffusion coefficient, D_e. High diffusion coefficient means high chloride ingress into concrete and cause to gradual loss durability of concrete. The result of effective diffusion coefficient is shown in Figure 7**.** It is clearly seen that the result of with cover and no cover of marine aquatic organism layer shows difference. Effective diffusion coefficient became large as increasing of W/B. Partial replacement of cement with by a combination of fly ash and the special admixture showed the best performance to reduce the effective diffusion coefficient. It appears that marine aquatic organism layer as concrete cover could reduce the effective diffusion coefficient. Effectiveness of marine aquatic organism layer for effective diffusion coefficient reduction in percentage is: sample A is 32.81%, sample B is 26.32%, sample C is 58.82%, sample D is 13.04%, sample E is 44.74% and sample F is 66.67%.

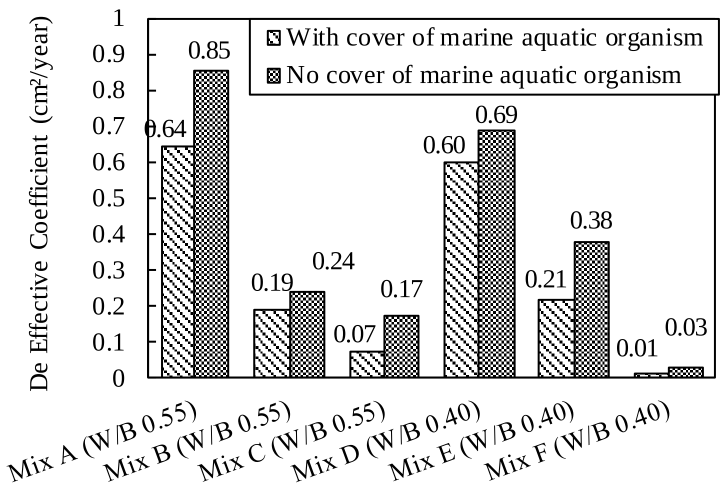


Figure 7. Effective chloride diffusion coefficient

Apparent diffusion coefficient, D_a. Figure 8 shows the result of apparent diffusion coefficient D_a, where the same result pattern can be seen as D_e result shown in Figure 7. In concrete that only uses OPC with different W/B, sample A (0.55: W/B) shows larger apparent diffusion coefficient than that of sample D (0.40: W/B). Partial replacement of cement with Fly Ash showed the best performance in decreasing the apparent diffusion coefficient.

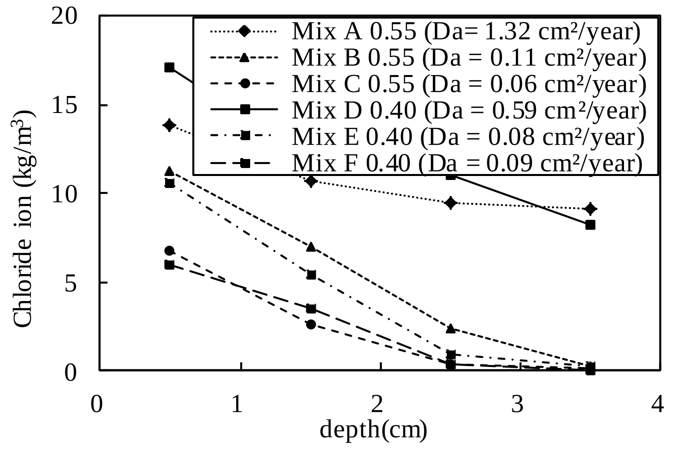


Figure 8. Apparent diffusion coefficient

Mercury Intrusion Porosimetry (MIP). Table 5 shows strength, porosity and distribution of pores in concrete. Pore size is divided into two categories, a capillary pores (0.01 – 5 μm) and a gel pores (<0.01 μm). Water to cement ratio affected the porosity of concrete as seen in Table 5. The higher the W/B is, the higher the porosity is, for sample A (0.55: W/B) and sample D (0.40: W/B). Blast Furnace Slag reduced pore volume inside concrete than the effect of Fly Ash. The special admixture shows the best performance to reduce pore volume, subsequently the permeability is reduced due to the capillary pores reduction in the concrete. In all of the tested samples, macro pores cannot be seen.

Compressive strength. Table 5 shows compressive strength after 13 years exposure in the marine environment. It can be seen that partial replacement of cement gave the positive effect. Concrete that only uses OPC with different W/B, Mix A (0.55: W/B) and Mix D (0.40: W/B) shows that compressive strength became larger as decreasing of W/B. On the other hand, concrete with mineral admixture shows the positive effect for larger long-term strength than OPC only, in the same W/B. A partial replacement of cement by a combination of Fly Ash and the special admixture showed greater long-term strength than mineral admixture and OPC only.

Table 5. Porosity, distribution pores of concrete and strength

Name	W/B	Comp. Strength (N/mm^2)	Total Porosity (%)	Porosity in pore size range (%)	
				Capillary pores 0.01 – 5 μm	Gel pores < 0.01 μm
A	0.55	44.74	19.30	8.61	10.69
B	0.55	64.26	21.56	6.33	15.23
C	0.55	59.43	36.84	11.47	25.37
D	0.40	70.64	17.82	6.17	11.65
E	0.40	67.38	12.93	4.16	8.76
F	0.40	79.20	21.33	7.11	14.22

CONCLUSION

Different level of W/B, partial replacement of cement with mineral admixture and marine aquatic organism layer affected the rate of chloride ion ingress into concrete. Based on investigation, the following conclusions are drawn:

1. Risk of corrosion increases as increasing of W/B and passivity film condition became worse as increasing of W/B. For mix A with 0.55 in W/B, the condition of passivity film became worst and corrosion area was about 17.87%.
2. Partial replacement of cement with fly ash maintains the passivity film on the reinforcing steel and also can reduce corrosion current in concrete under marine condition.
3. Covering of marine aquatic organism layer on concrete surface reduced the rate of chloride ingress and chloride diffusion coefficient.

ACKNOWLEDGMENT

The authors would like to express their gratitude to The Port and Airport Research Institute of Japan, which has kindly offered the sample for this study. Thanks are also extended to Center of Advanced Instrumental Analysis in Kyushu University.

REFERENCES

Hamada, H., Sagawa, Y., Ikeda, T., and Morikawa, R. (2010). "Several Factors affecting the anodic polarization curve of steel bars embedded in mortar." *Concrete under Severe Conditions*, Vol. 1, 201-208.

Liu, P. C. (1991). "Damage to Concrete Structure in a Marine Environment." *Material and Structures*., 24, 302-307.

Nakamura, E., Watanabe, H., Koga, H., Nakamura, M., and Ikawa, K. (2008). "Half-cell Potential Measurements to Asses Corrosion Risk of Reinforcement Steels in a PC Bridge." *Symposium on Site Assessment of Concrete, Masonry and Timber Structures.,* 1, 109-117.

Nemati, K. M. (1997). "Fracture Analysis of Concrete Using Scanning Electron Microscopy." *Scanning.,* 19, 426-430.

Tang, L., and Sorensen, H. E. (2001). "Precision of the Nordic test methods for measuring the chloride diffusion/migration coefficients concrete." *Material and Structures*, 34, 479-485.

Otsuki, N. (1985). "A study of effectiveness of Chloride on Corrosion of Steel Bar in Concrete." *Report of Port and Harbour Research Institute*, 127-134.

Watanabe, H., Iwanami M., Hamada H., and Yokota, H. (2002). "A Study on Durability Enhancement of Marine Structures Covered with Marine Aquatic Fouling Organism." *Report of the Port and Airport Research Institute*, 41: 3.