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Durability of Various Anti-Corrosive Organic Coatings in Marine Environment for Twelve Years

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In order to clarify the durability of protective coatings for maritime steel structures, various anti-corrosive organic coated steel samples were exposed for twelve years in semitropical marine environment at Miyakojima Island, Okinawa, JAPAN. Samples were various organic coated steel pipes, 4.0 m in length and 150 mm in diameter. While the bare steel pipe entirely corroded in 4.5 mm thickness in four and half years, these organic coated steel pipes exhibited protective appearances after twelve-year-exposure except for the defect in the coatings. Polyethylene (PE) lining pipe exhibited a good protective performance. Urethane painted pipe was also good but some barnacles stuck to its surface. A combination of petrolatum tape and FRP cover showed sufficient corrosion resistance for steel surface. The correlation in results between exposure and laboratory acceleration test was examined. It was found that salt spray test (SST) results corresponded to rusted area of scratched portion and that adhesion change of coating layer corresponded to the rotating immersion test result. Among the on-site measured data, volume resistivity is utilized for the index of corrosion protection performance of organic coating.

Keywords : *organic coating, marine environment, corrosion protection, durability*

1. Introduction

Recently, many structures were built in marine environments and the organic coatings were widely used for protecting them. Various types of products for protective coatings were introduced and utilized until now. Although the characteristics of these organic materials were shown in their catalogues, the compared data of the protective performance with each other is not available.

In order to get these compared data, several exposure tests have been carried out.[1)-3)] Harada *et al.* introduced 15-year-exposure results of some organic coated steel pipe piles in Philippine. They concluded that the comparatively large portion of organic coated steels had good protective performance but the damaged portions were less protective. And they also pointed out that the polyethylene-lining pipe underwent no damage during fifteen years exposure.[2)]

Another approach to evaluate the durability of the organic coated steels is accelerated test in the laboratory. Yamamoto *et al.* introduced a technique to estimate the service life of glass flake reinforced epoxy coatings using electrolysis in seawater.[4)] The other methods using electrochemical measurement was introduced for evaluation of paint performance.[5)-7)] Such application was mainly concerned about the correlation between the electrochemical results and the results of short time exposure. The comparison between laboratory results and the long-term exposure tests is important and these results may lead to the estimation of service life of organic coatings.

In this report, the exposure results are introduced and relationships between accelerated tests or monitoring results and exposure results are discussed.

2. Experimental

2.1 Exposure site

An exposure site is located at Miyakojima Island, Okinawa prefecture in Japan (latitude; 25.27 N and longitude; 125.17 E). The average temperature is 23.3℃ and average relative humidity is 78 %. The sample stands were fixed at the inner wall of a breakwater in Hirara bay.

2.2 Samples

The exposed samples listed in Table 1. A bare steel sample was tested for 4.5 years and retrieved because this sample heavily corroded and structural damage occurred. The other samples were exposed for 12 years.

Table 1. List of exposed samples

Code	Specification	Thickness (μm)	Number of Sample
SS	Bare steel (4.5yeras)	-	1
CE	Coal tar epoxy	800	1
IZ/CE	Inorganic zinc/ coal tar epoxy	250-400	3
IZ/E	Inorganic zinc/ epoxy	250-300	4
IZ/V	Inorganic zinc/ vinyl	300	2
IZ/LE	Inorganic zinc/low temperature curing type epoxy	300-350	4
IZ/U	Inorganic zinc/urethane	2000	1
OZ/U	Organic zinc/urethane	2000	1
OZ/GP	Organic zinc/glass flake reinforced paint	1500	1
GP	Glass flake reinforced paint	1500	3
PE	Polyethylene lining	3000	3
FRP	Petrolatum tape with FRP cover	5000	1

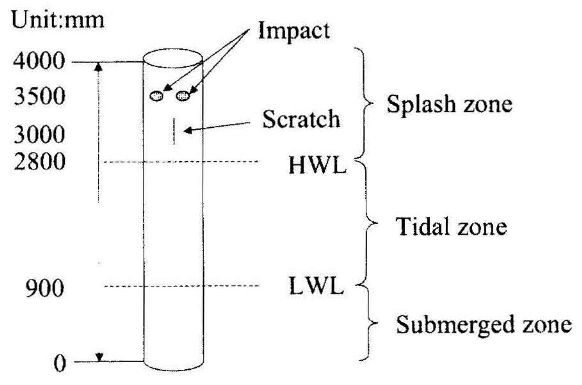

Fig. 1. Schematic illustration of exposed samples

Fig. 1 shows a schematic illustration of the samples exposed. The mild steel pipes, 150 mm in diameter, 4,000 mm in length and 4.5 mm in thickness were used. These samples were grid blasted and organic coated with various types of organic coating system listed in Table 1. The column named number of sample means the number of samples coated with the same resin type of different products. All coating procedures were carried out according to their recommended conditions.

Two impact marks were created by dropping 2 kg or 4 kg steel ball from 1 m height. A 300 mm long scratch mark penetrated through organic coating layer was made by rotating disk grinder. These damaged portions were located at the splash zone. Mean high water level (HWL) and mean low water level (LWL) are described in Fig. 1. Thus the length of tidal zone is about 1.9 m. The coupon samples, 150 x 75 x 4.5 mm size, were also made in the same conditions as those for pipe samples for laboratory accelerated tests.

2.3 Initial data

Some initial data were measured in each sample. Thickness of coating layer was measured by electro-magnetic thickness gauge. Resistivity of coating layer was measured in 500 V in applied voltage, 40X40 mm in measured area. Measured resistance was reduced to resistivity per unit volume. Initial adhesion strength of coating layer was measured at 6 points of coupon samples and averaged.

2.4 Laboratory acceleration test

Three laboratory acceleration tests were carried out.

1) Salt spray test (SST); Test solution was 5% NaCl aqueous solution. Test temperature was 35 ℃.

2) Immersion Test; Test solution was 5% NaCl aqueous solution. Test temperature was 40 ℃.

3) Rotating immersion test; Samples attached to the rotating holder were immersed in aerated 5% NaCl aqueous solution. Diameter of the holder was 1.0 m and rotating speed was 5 cycles per minute. The flow velocity of sample surface was 31.4 m/min in this condition.

All tests proceeded for 3 months.

2.5 On-site measurement

On-site measurements were performed at 1, 3, 4.5, 10 years after samples setup. In each on-site measurement, visual observation, hardness of coating, volume resistivity and AC impedance measurements were carried out. The AC impedance data scattered very much, thus these data were not adopted in this report.

2.6 Evaluation after exposure

After exposure for 12 years, the samples were investigated with visual observation and measurement of rusted area at damaged portions. Pull-off adhesion tests were carried out at the tidal and the submerged zone of exposed samples. The adhesion strength of PE could not be measured because adhesive delaminated at film/adhesive interface. Change in adhesion strength during exposure test, Δ adhesion strength, was calculated from the average value of initial measurements of coupon samples and the exposed samples' data.

3. Results and discussion

3.1 Corrosion rate for bare steel

The bare steel sample exposed for 4.5 years was cut into small pieces and then residual thicknesses of them were measured with micrometer. Corrosion rate was calculated from remainder and initial thickness (4.5 mm). The average corrosion rate of each portion is shown in Fig. 2.

The corrosion rate of the submerged zone was about 0.13 mm per year. This value was not so different from previously reported data.[8] The corrosion rate of the upper part of the tidal zone was close to that of submerged zone. The corrosion rate of lower part was larger than that of upper part in the tidal zone. It is attributed to the effect of macroscopic electrochemical cell. The corrosion rate of the splash zone showed about 0.8 mm per year. This value was very much greater than that of previously reported data.[8] It is estimated that the effect of splash of seawater in this exposure site is severer than that in the reported site. The damaged portions of coatings with scratch or impact were located in this severely corrosive region.

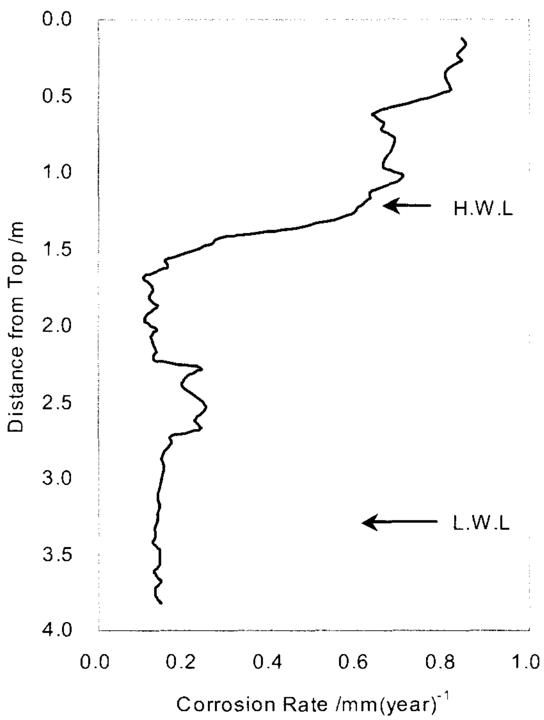

Fig. 2. Corrosion rate of bare steel pipe

3.2 Visual observation of exposed samples

The results of visual observation are summarized in Table 2. The impact portions heavily rusted in many samples except for the PE. The scratched portions rusted in most cases. Among them, better corrosion protections were observed at scratched portion in IZ/U, OZ/U and OZ/GP. Almost all samples exhibited good corrosion resistances in the splash zone. CE and IZ/CE partially rusted in the tidal and submerged zone. Many blisters existed on coating film in CE and some blisters were observed in IZ/CE and IZ/E. IZ/V rusted at the tidal and submerged zone. IZ/LE rusted at tidal zone. Interlayer delamination was observed in IZ/V and IZ/LE. Then corrosion occurred at those delaminated portions.

IZ/U and OZ/U also rusted in tidal zone. Many barnacles stuck to these surfaces and some of the stuck portion rusted.

OZ/GP and GP exhibited a good appearance, but underfilm corrosion were observed after removal of coated layer.

PE rusted at scratched portion but the other portions exhibited a very good corrosion resistance. FRP exhibited a good appearance and corrosion was not observed at the steel surface after removal of the petrolatum tape.

3.3 Rusted area and change in adhesion

A rusted area of damaged portion was measured after removal of coating and rust layer. Fig. 3 shows rusted areas at the ball impact portion and Fig. 4 shows those at the scratched portion. One typical sample in the same resin group is plotted in the fig.

PE did not rusted at ball impact portion. IZ/LE exhibited a good corrosion resistance at the impact and scratched portions. OZ/GP and GP severely rusted at the impact portion. It is recognized that these coatings had hard and brittle natures and many micro cracks were introduced in the impacted portion and then corrosion occurred through these micro cracks. By comparing IZ/U with OZ/U, it is obvious that inorganic zinc primer exhibited a better corrosion resistance than organic zinc primer.

Fig. 5 shows a change in adhesion strength during exposure test. When Δ adhesion strength is larger than zero, it means the adhesion strength increased during

Table 2. Outlook observation of coated samples

Code	Number of Samples	Impact	Scratch	Splash	Tidal	Submerge	Remarks
CE	1	R	R	S	M	M	Many blisters
IZ/CE	3	R	R, M	S	M	M	Some blisters
IZ/E	4	R	R	S	R, M	S, M	Some blisters
IZ/V	2	R	R	S	R	R	Interlayer delamination
IZ/LE	4	R	R	S	R	M	Interlayer delamination
IZ/U	1	R	M	S	R	M	Many barnacles' pits
OZ/U	1	R	M	S	R	S	Many barnacles' pits
OZ/GP	1	R	M	M	M	S	Underfilm Corrosion
GP	3	R	R	S, M	S, M	S, M	Underfilm Corrosion
PE	3	S	R	S	S	S	Good except scratch portion
FRP	1	-	-	S	S	S	Good

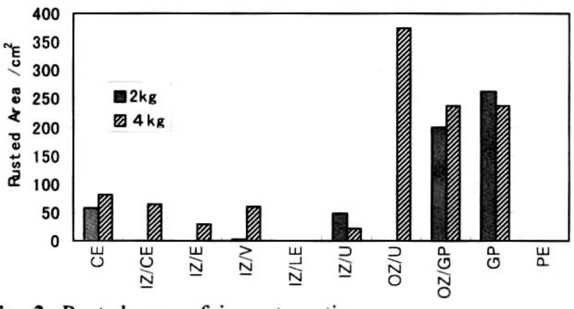

Fig. 3. Rusted area of impact portion

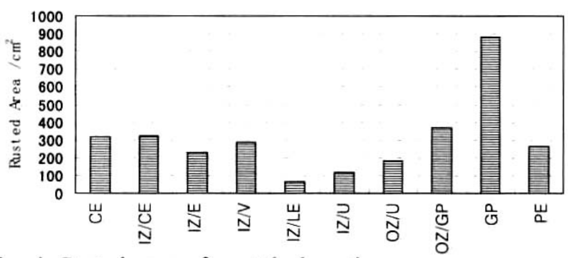

Fig. 4. Rusted area of scratched portion

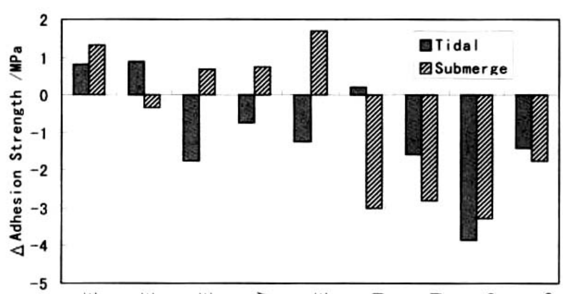

Fig. 5. Change in adhesion strength during exposure test

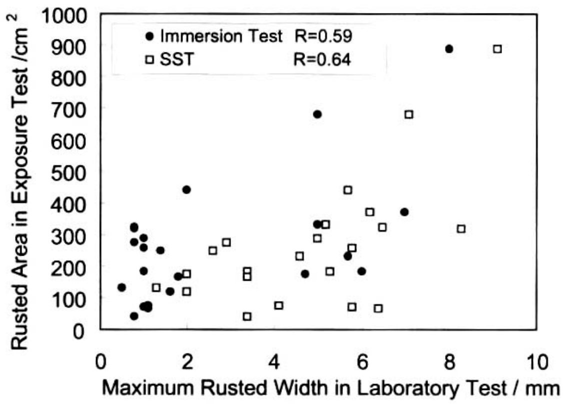

Fig. 6. Relationship in rusted area between exposure and Laboratory test

exposure periods. And it is less than zero, it means the adhesion strength decreased. Adhesion strength increased in whole epoxy type coatings at the submerge zone and it increased at the tidal zone in coal tar epoxy coating samples. Adhesion strength decreased at all portions in OZ/U, OZ/GP and GP. It is estimated that degradation of coating layer occurs in these samples.

3.4 Relationship between exposure results and acceleration tests

Relationships between exposure tests and laboratory acceleration tests were investigated and some significant results were obtained. Typical two results are shown in Fig. 6 and 7. Fig. 6 shows relationships in rusted area between exposure and laboratory test. Though some scattering data existed, two correlations between exposure and laboratory test were found. One was a correlation

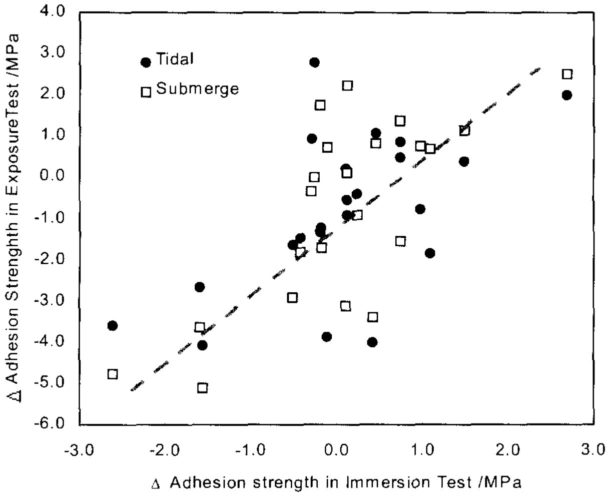

Fig. 7. Relationship in Adhesion strength between exposure and rotating immersion test

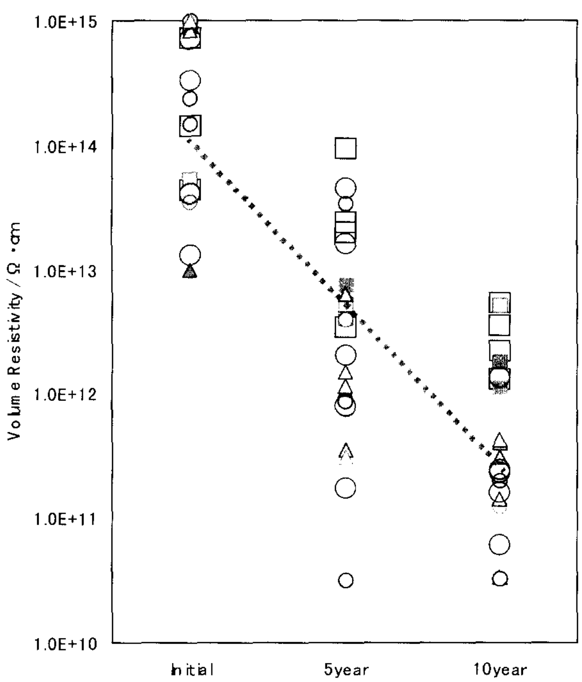

Fig. 8. Change in volume resistivity during exposure period.

between exposure and immersion test and correlation coefficient (r) was 0.59 and another was that between exposure and SST and its r was 0.64. Fitness test of t-value indicated that these two correlation coefficients were significant in 99% significance level. The correlation coefficient of SST was slightly greater than immersion test. Thus, SST is better evaluation method for scratched portion at the splash zone.

As for Δ adhesion strength, correlation between the exposed sample and the rotating immersion test was found (Fig. 7). The correlation coefficients of these relationships were 0.75 for tidal and 0.72 for submerge zone, respectively. And these values were 99% significant level from fitness test using t-value. Thus, rotating immersion test can be used for the acceleration test of adhesion change in organic coating sample.

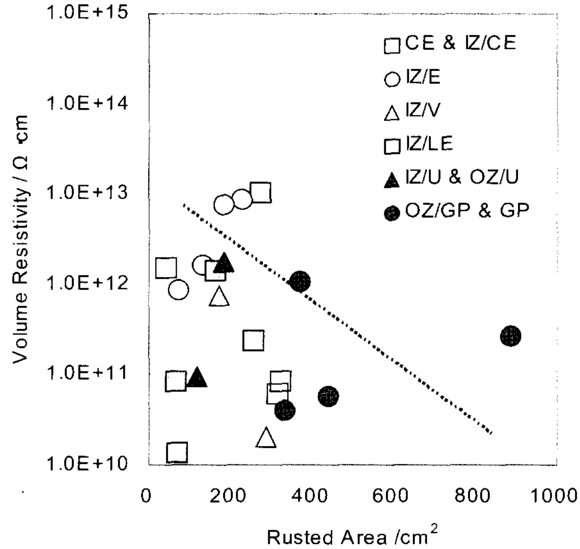

Fig. 9. Relationship between rusted area and volume resistivity.

3.5 Relationship between exposure results and on-site measurements

Relationship between exposure results and on-site measurements were investigated. Among the on-site measurements, data of volume resistivity correlated with exposure results, especially rusted area at the scratched portion. Fig. 8 shows a change in volume resistivity during exposure period. Volume resistivity decreased with exposure time in all samples. Fig. 9 shows a relationship between volume resistivity and rusted area at scratched portion. There exists weak correlation in logarithmic volume resistivity and rusted area. In the on-site measurement data, volume resistivity is utilized for a degradation index of organic coatings.

4. Conclusions

1) While the bare steel sample entirely corroded in 4.5 mm thickness in four and half years, various organic coated steel samples exhibited protective appearances after twelve-year-exposure.

2) PE lining sample exhibited a superior protective performance except for damaged portion.

3) Low temperature cured type epoxy coated samples

exhibited a good corrosion resistance at the impact and scratched portions.

4) Some barnacles stuck to the surface of urethane painted sample.

5) Grass flake reinforced paint coated samples heavily corroded at the impact portion.

6) Inorganic zinc primer exhibited a better corrosion resistance than organic zinc primer.

7) A combination of petrolatum tape and FRP cover showed sufficient corrosion resistance.

8) Among the laboratory acceleration test, SST results corresponded to rusted area of scratched portion and rotating immersion test corresponded to adhesion change of coating layer.

9) Among the on-site measurement data, volume resistivity is utilized for a degradation index of organic coatings.

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