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Study on the Corrosive Characters of Carbon Steel in the Marine Splash Zone

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This study determined that the four corrosive characters of carbon steel in the marine splash zone (MSZ) in China's four sea areas. It has a range and a corrosion peak value. The rust in the MSZ plays the role of "depolarizer" in the cathodic process of corrosion. The growth law of the rust layer in MSZ has a character of "annual ring". In addition the reasons causing serious corrosion of carbon steel in the marine splash zone has been discussed in this paper.

Keywords *: carbon steel, marine splash zone, corrosive characters*

1. Introduction

Since the concept of marine splash zone (MSZ) was first proposed by Humble, Many researches proved that the corrosion of iron and steel in the splash zone is the most serious in the marine environment[1] and that this MSZ corrosion has a peak.[1] However the environmental factors causing the corrosion peak was not known then[2)-3)] and the range of the MSZ was not yet clearly defined.[4]

This paper explains the corrosive characters of iron and steel in the MSZ, the main cause of the corrosion peak and defines the exact range of the MSZ in some of China's harbors. Besides, This paper discusses the growth law of rust layer

This paper make it clear that the corrosive characters of iron and steel in the MSZ and provide reference for the study of new materials and suitable anticorrosive methods.

2. Experimental

1) Groups of carbon steel samples (electric- joining) were set vertically 0-2.8 m above the mean high water level (M.H.W.L) of the seawater in the harbors of Qingdao, Zhoushan,Xiamen and Zhanjiang in order to determine the range of the MSZ, the location of the MSZ corrosion peak, the corrosion rate of carbon steel samples over time, and the effect of marine and meteorological conditions on the corrosion.

2) The salt particle deposits on the samples were analyzed and the sample's surface water film's electrochemical character (as revealed by the corrosion current Vs time curve) was determined with a type ACM-1512B atmospheric corrosion monitor.

3) The effect of rust on the cathodic process of corrosion in the MSZ was studied under deoxidization condition.

4) Groups of carbon steel samples were set vertically on testing rack of MSZ in Qingdao, in order to determine the corrosion rate of different season and survey the feature of the rust layer in different time.

3. Results and discussion

The results of this two-year study on the corrosion of carbon steel in four typical sea areas are presented in Figs. 1-7, Table 1and discussed below:

(1) About the range of MSZ-(the corrosive characters 1).

Fig. 1 on the corrosion of carbon steel in the splash zone in four sea areas shows that the MSZ was 0-2.4 m above the M.H.W.L.

For the MSZ of harbor in China, it is to say the location of iron and steel structures above M.H.W.L. of seawater 0-2.4 m is the most serious location of marine corrosion undergo the strike of seawater plash (or small particle) and the sunshine, under wet/dry cycle conditions.

The MSZ undergo the corrosive environment of sea salt particle under wet/dry cycle conditions is similar to the marine atmosphere zone, but it's more serious (see Fig. 2a). Fig. 2b shows the water film's electrochemical character on MSZ and atmospheric zone. .

(2) Forming of corrosion peak in MSZ-(corrosive characters 2).

From Fig. 1, the corrosion of iron and steel prevails a corrosion location of the most serious in MSZ-the

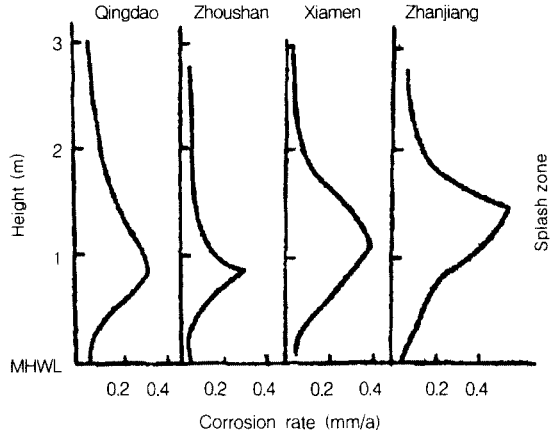


Fig. 1. Corrosion of carbon steel (long sample) in splash zone (in four sea ureas)

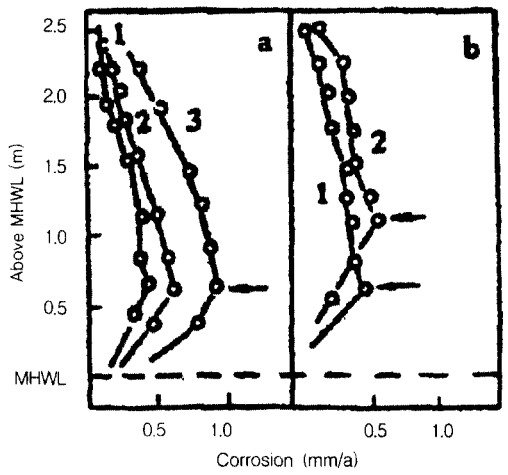


Fig. 3. Corrosion of carbon steel in splash zone (Qingdao sea aren)
a. 1. one year, 2. half year, 3. three months
b. 1. in harbour, 2. in open sea, ↑ peak value

corrosion peak, and that local marine and meteorological conditions determined the rate ,whose peak located about 0.6-1.2 m above the M.H.W.L.

Fig. 3 shows that the corrosion rate decreased with exposure time span, but varied little under the same experimental condition, and the location and date of the corrosion peak rises in open sea. The range of MSZ was extended in this situation.

Fig. 4 shows the corrosion current (as measured with the probe of the Fe-Zn cell of the atmospheric monitor) against time curve of the sample in the corrosion peak of MSZ during wet and dry conditions. "+0.5" mean by above the peak value 0.5m.

Fig. 5 shows the salt particle content in the MSZ corrosion peak (MSZCP) and nearby area. From Fig. 4 and Fig. 5 the salt particle content on surface of steel and the corrosion current in the MSZCP were greater than other areas.

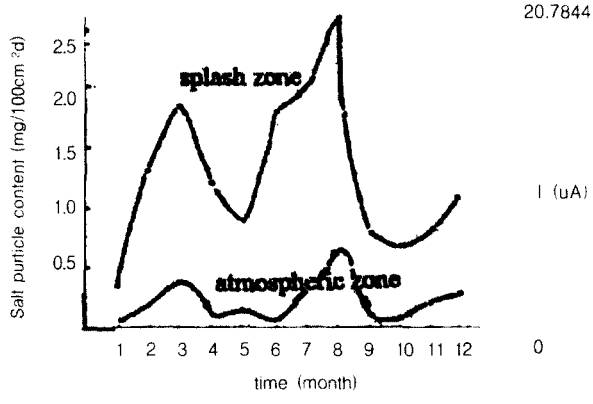
(3) The action of rust in MSZ- (corrosive characters 3) .

Fig. 6 gives the polarization curve of the steel sample with rust at the MSZ in seawater under oxidation and deoxidization conditions. It shows the rust in the MSZ plays the role of "depolarizer" in the cathodic process of corrosion, because the cathodic current of the rust sample in the MSZ under deoxidization condition is smaller than that without deoxidization but exceeds by far that of the no-rust sample in the MSZ under deoxidization condition.

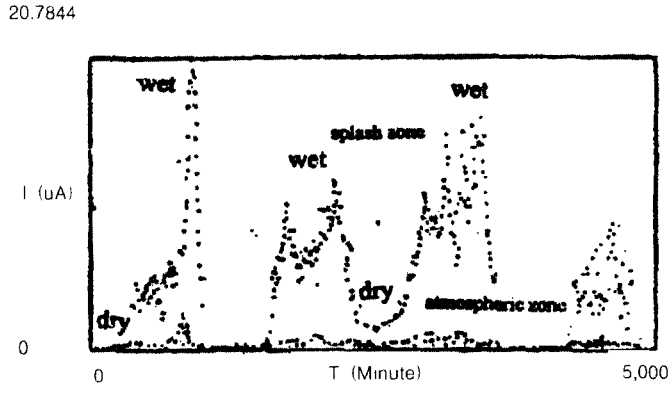
The results are similar with the reductive process of rust layer.[4)-5)]

(4) The growth law of rust layer in MSZ[6)]-(corrosive characters 4)

The corrosion rate of carbon steel in Qingdao MSZ in



a. varying of salt particle content



b. corrosion current-time curve

Fig. 2. The comparison of marine splash zone and atmospheric zone

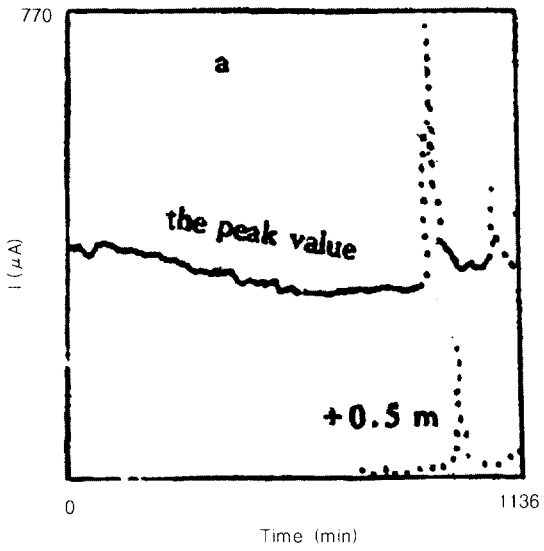


Fig. 4. Corrosion current-time curve in the corrosion peak

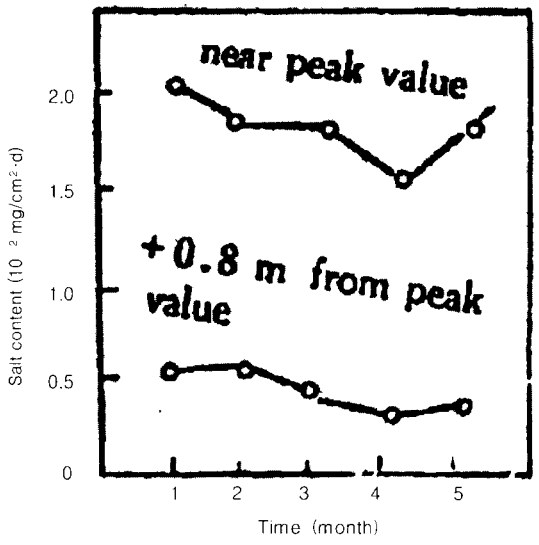


Fig. 5. Salt particle content in splash zone

Table 1. corrosion rate of carbon steel in the Four seasons of MSZ in Qingdao

Seasons	Spring	Summer	Autumn	Winter
Testing time	15/3-15/6	15/6-15/9	15/9-15/12	15/12-15/3
Mean corrosion rate (mm/a)	0.8618	0.7511	0.1484	0.1221

different season is shown in Table 1.

Fig. 7 shows the different feature of carbon steel sample under various years of expose. The rust layers pose the character of "annual ring" The rust layer grows every year, but the thickness is different. The rate of corrosion

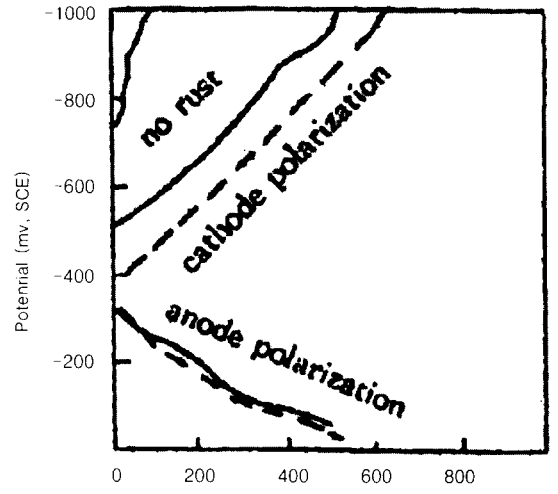


Fig. 6. Polarization curve of rust in seawater (5months in splash zone) ——dcoxidation, --------non-deoxidation

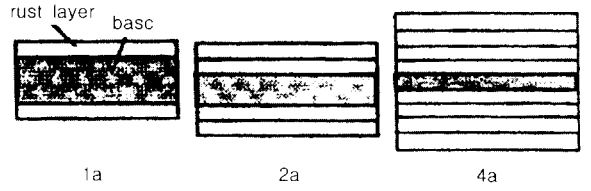


Fig. 7. Rust (layered structure) of MSZ (schematic diagram)

decrease, the thickness of "annual ring" become thinner. Table 1 shows that the corrosion rate of carbon steel is higher in spring than in winter. It indicates the corrosion in winter is less and it probably grows layer in spring.

The X-ray analyses indicates that the rust layer of carbon steel compose of α FeOOH, β FeOOH, γ FeOOH and Fe_3O_4, among them γ FeOOH has the most larger quantity, they scatter intermittently and have a lot of cracks and holes. There are a lot of (Fe_3O_4) in inner rust layers. Because the γ F_3O_4 has electric conductivity. It is beneficial to the electrochemical process. Why the rust layer was separated from between layer upon layer? It can be analysis from the process of rust steel in MSZ. What with the cracks and trickle are produced during the process of wet and dry cycle. Oxygen spread quickly into the rust layer make γ F_3O_4 re-oxidation. What with such process carried on for several times, to form the cycling of "oxidation-reduction-re-oxidation". Additionally physical character is different in inner or outer layer in addition the influence of the environmental factors. Gradually the rust layers which easy to strip off and the layered structure was formed.

Thus it can be seen that the main environment factors causing serious corrosion of carbon steel in MSZ are the

large accumulation of salt particles at the steel surface and the high frequency dry and wet environmental conditions.

The surface of the carbon steel in the MSZ is subject to intense oxygen and rust depolarization so the corrosion here is accelerated, and a corrosion peak occurs.

4. Conclusions

The corrosion of carbon steel in the MSZ has four characters.

1) The MSZ has a definite range, which depends on the local marine and meteorological condition.

2) The MSZ has a corrosion peak.

3) The rust of carbon steel in the MSZ that can reduce and transform, the rust plays role of "depolarizer" in the cathodic process of corrosion.

4) The growth of the rust layer of carbon steel in the MSZ has a character of "annual ring" in the harbour of four seasons clearly.

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