CORROSION OF CONSTRUCTION METALS UNDER SIMULATED ACID RAIN/FOG CONDITIONS WITH HIGH SALINITY

H. H. P. FANG, K. K. WU, and C. L. Y. YEONG

Civil and Structural Engineering Department University of Hong Kong, Pokfulam Road, Hong Kong

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Abstract. Corrosion of 1,312 specimens of five common construction metals were examined in a salt-spray chamber under simulated conditions of acid rain/fog with high salinity. When specimens were exposed to a condition simulating the acid rain/fog during summer in Hong Kong, i.e. pH 3.5, 1% of salt and 35 °C, the average corrosion rates were 735, 330, 2, 97 and 9 μm yr^{-1}, respectively, for mild steel, galvanized steel, stainless steel 304, red brass and aluminum. Relative effects of pH, salt concentration and temperature on the corrosion of these five metals were analyzed based on tests conducted at nine designed conditions. For the first four metals, the corrosion rate appears to increase linearly with the increase of 'acidity', salinity and temperature, according to regression analysis. Corrosion rate of SS 304 is almost independent of salinity and temperature, but is slightly affected by pH. Red brass is more susceptible than SS 304, but its susceptibilities to pH and salinity are one order of magnitude lower than those of mild steel and galvanized steel. Mild steel is about five times more susceptible to pH than galvanized steel; whereas the latter is about three times more susceptible to salinity than the former. Aluminum's corrosion rate increases as pH decreases; however, the effects of salinity and temperature are inconclusive.

1. Introduction

Estimates of annual corrosion damage vary from 0.19 to 3.0% of GNP in the United States, i.e. \$ 8 to \$ 126 $\times$ 10^9 (Fontana, 1986), to 3% of GNP in the United Kingdom (Manning, 1987). Although its cost has never been quantified, corrosion in Hong Kong is believed to be even more severe than that in most of the industrial countries.

It is well known that acidity, heat and salt in rain/fog cause severe corrosion to construction materials. In Hong Kong, only a small fraction of its 1070 km^2 of mountainous territory is inhabited by 5.7 $\times$ 10^6 people. In this congested city by the South China Sea, air is heavily polluted by the coal-burning power stations, exhaust gas from motor vehicles and thousands of small factories burning low cost fuels with S content as high as 3%. This results in perennial acid rain and fog with an acidity as low as pH 3.4. In addition, because its subtropical climate and its proximity to sea, the acid rain/fog in Hong Kong also has high temperature and contains high levels of salinity.

This study was conducted to examine the corrosion rates of five common construction metals when exposed to a condition which simulated the acid rain/fog during summer in Hong Kong. Metal specimens were exposed to atomized acid solution in a constant temperature chamber. The rate of corrosion of each specimen was calculated from its weight loss after the exposure and the duration of the test.

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Also examined in this study were the individual effects of pH, salinity and temperature on the relative corrosion rates of these metals. These tests were conducted under accelerated testing conditions. The levels of pH, salinity and temperature of each test condition were based on the two-level factorial design (Box and Hunter, 1961; Chian and Fang, 1975).

2. Methods and Materials

Selection of metals

Three ferrous metals and two nonferrous metals commonly used in construction were selected for this study, including mild steel, galvanized steel, stainless steel type 304 (SS 304), red brass and aluminum.

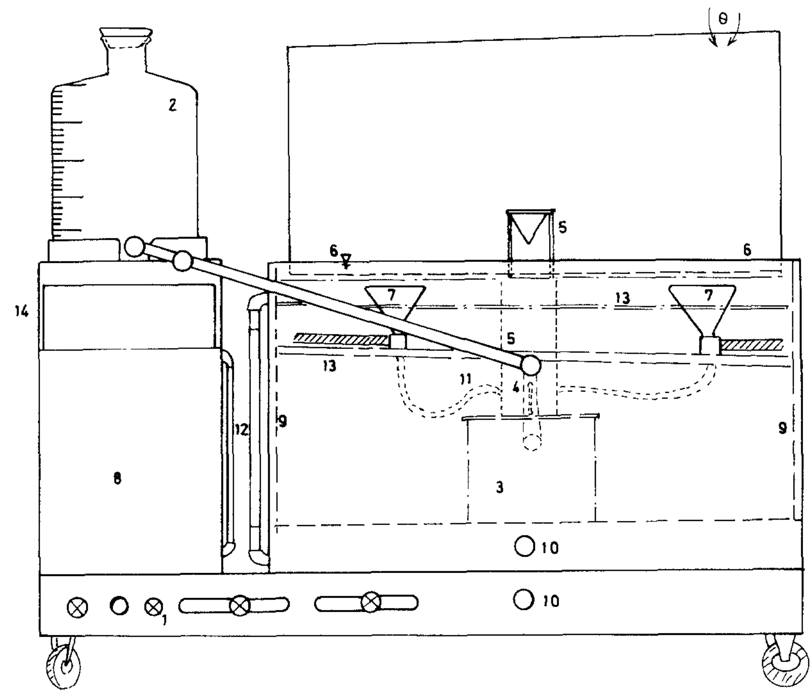
Among the five metals, mild steel is most widely used for construction, because of its strength, weldability and low cost. But, it is also most vulnerable to corrosion. Mild steel normally contains less than 0.5% of C; however, the C content in most cases does not affect the corrosion rate (Fontana, 1986). Galvanized steel is steel coated with a thin layer of Zn, which is used as a sacrificial metal for cathodic protection of steel. It is commonly used for piping, fencing, nails, etc. Zinc does not have good corrosion resistance. However, when the Zn coating is corroded, it forms a layer of oxide on the surface and provides the steel with some protection from the environment. SS 304 is the most widely used stainless steel. It contains 18% Cr and 8% Ni, and exhibits excellent resistance to corrosion. It is very expensive as compared to other construction metals.

Red brass is an alloy containing 85% Cu and 15% Zn. Copper itself has excellent weathering resistance. It has been used for external service, such as roof top, for several hundred years. An economic comparison was made (Fink *et al.*, 1971) for several metals used in roofing, including copper, galvanized steel and terneplate. Results showed that Cu, although having the highest installation cost, had the lowest cost of service per unit area. In most cases, a copper roof would outlast the service life of the building it protects. Zinc is added to enhance the strength of Cu. However, it weakens the resistance to corrosion, especially in the presence of chloride and sulfate.

Aluminum is the second most widely used metal in external use, only after steel. It not only has a high degree of resistance to environmental attack, but also has many other desirable characteristics, such as favorable strength-to-weight ratio, ease of fabrication and attractive appearance. When it is exposed to atmosphere, aluminum forms a thin but dense coating of aluminum oxide, protecting the aluminum from corrosion.

Simulation of acid rain/fog

Thin metal specimens with a size of 20×40 mm were first cleaned in solution to remove the surface grease and rust using procedures as specified by the American



θ: angle of lid, 100°
1: air inlet
2: salt solution reservoir
3: internal reservoir
4: spray nozzle
5: dispersion tower
6: water seal
7: fog collecting device
8: air saturator and heater
9: water jacket
10: combination drain and exhaust
11: measuring tube
12: water level indicator
13: supports for specimens
14: control panel

Fig. 1. Salt-spray (fog) chamber for corrosion tests.

Society for Testing and Materials (ASTM, 1987). After cleaning, specimens were weighed and then hung on rods at different locations in a constant temperature chamber. The design of the chamber, which is illustrated in Figure 1, and the handling procedures of the specimens followed the detailed ASTM specifications (1987). Water solution with controlled pH and salinity were atomized by the spray nozzle in the chamber, forming acid rain/fog at 100% relative humidity at the designed pH, salinity and temperature.

At the end of the test period, metal specimens were cleaned once more using the same procedures to remove the corrosion products, and then weighed. The corrosion rate of each specimen, as expressed in $\mu m\ yr^{-1}$, was calculated from the weight loss, with the knowledge of the density and surface area of the specimen and the duration of exposure. For each test condition of pH, salinity, temperature

and duration, four to seventeen specimens of each metal were examined to check the reproducibility of the corrosion rate measurement.

In this study, the salinity in acid rain/fog is represented by the sodium chloride concentration (%) in the water solution. The pH is adjusted by the addition of H_2SO_4 in the water solution. In Hong Kong, SO_2 is the major source of acidity in acid rain/fog. It is rapidly absorbed by water droplets in the atmosphere, forming H_2SO_3, which could be further oxidized to form the stronger H_2SO_4.

Test condition of two-level factorial designed experiments

Three independent environmental parameters, i.e. pH, salinity and temperature, were chosen for this study. A total of nine experimental conditions in eleven tests were designed for this study. The two-level factorial design (Box and Hunter, 1961; Chian and Fang, 1975) requires eight experimental conditions at the upper and lower levels of each of these three parameters, as shown in Figure 2. The lower and upper levels were respectively selected as 2.5 and 3.5 for pH, 1 and 6% for salinity, and 35 and 45 °C for temperature. A ninth condition was selected at the mid-levels of each variable, i.e. pH 3.0, 3.5% salt and 40 °C. Three tests were conducted at this condition to determine the reproducibility of corrosion measurement at the same condition.

The mildest of the nine test conditions, i.e. pH 3.5, 1% salinity and 35 °C, was

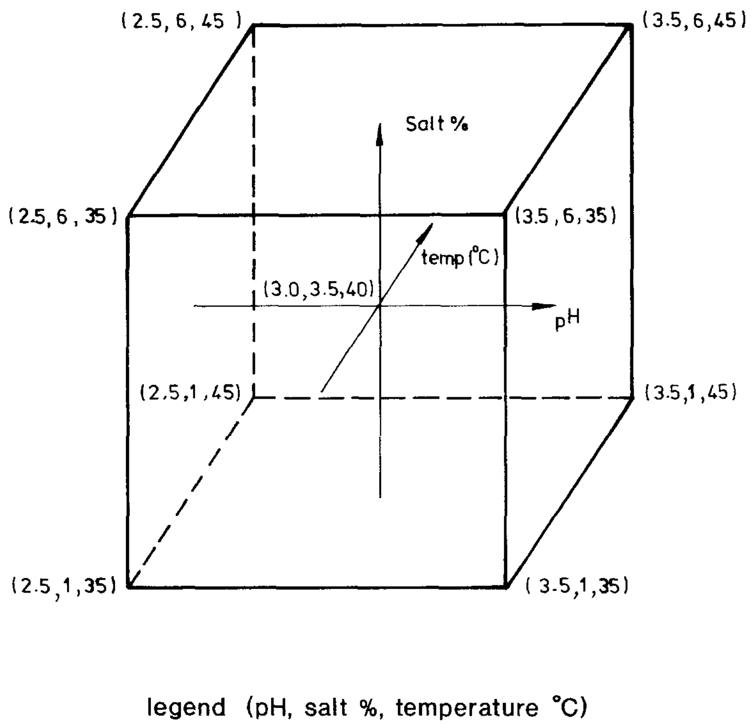


Fig. 2. 2^3 factorial design of experiments.

to simulate the condition of acid rain/fog during summer in Hong Kong. The other eight test conditions are unlikely to be found in the acid rain/fog. Experiments were conducted, however, at those conditions to accelerate the corrosion in order to compare the relative effects of pH, salinity and temperature on the differrent construction materials.

3. Results and Discussion

The corrosion rates of 1312 metal specimens (20 × 40 mm) were examined in eleven tests. At each test, about 60 specimens were examined after 48 hr, whereas the other 60 specimens were examined after 120 hr. Among the 60 metal specimens, four specimens were mild steel, five were aluminum, and seventeen each were galvanized steel, SS 304 and red brass. The average corrosion rates for mild steel, galvanized steel, SS 304, red brass and aluminum at each condition are summarized in Tables I to V sequentially. Also shown are the corresponding standard deviations of the corrosion rates at each condition.

Reproducibility of corrosion rate measurements

The 'ratio' columns in Tables I to V show the ratio of standard deviation to the average measurement at each test condition. The smaller the ratio, the higher the reproducibility of the measurement in the chamber for a given test. In general, the reproducibility for a given metal did not vary much, regardless the test condition and duration. It however depends mainly on the metal. The overall averages of the ratio vary from about 5% for mild steel, 10% for red brass, 15% for galvanized

TABLE I

Average corrosion rates and the standard deviations of mild steel

Conditions			48 hr test				120 hr test			
	Salt	Temp								
pH	(%)	(°C)	No. of sample	Avg. μm yr^{-1}	St dev μm yr^{-1}	Ratio (%)	No. of sample	Avg. μm yr^{-1}	St dev μm yr^{-1}	Ratio (%)
2.5	6.0	45	4	1411	91	6%	4	1341	61	5%
2.5	6.0	35	4	1176	92	8%	4	999	59	6%
2.5	1.0	45	4	1298	130	10%	4	1147	32	3%
2.5	1.0	35	4	1132	47	4%	4	1064	29	3%
3.5	1.0	35	4	853	31	4%	4	735	47	6%
3.5	1.0	45	4	939	16	2%	4	701	7	1%
3.5	6.0	35	4	994	67	7%	4	883	55	6%
3.5	6.0	45	4	909	27	3%	4	833	39	5%
3.0	3.5	40	4	1048	91	9%	4	1062	30	3%
3.0	3.5	40	4	1067	66	6%	4	1050	59	6%
				Average of 10 tests = 6%.				Average of 10 tests = 4%.		

TABLE II

Average corrosion rates and the standard deviations of galvanized steel

Conditions			48 hr test				120 hr test			
pH	Salt (%)	Temp (°C)	No. of sample	Avg. μm yr^{-1}	St dev μm yr^{-1}	Ratio (%)	No. of sample	Avg. μm yr^{-1}	St dev μm yr^{-1}	Ratio (%)
2.5	6.0	45	17	710	102	14%	17	605	110	18%
2.5	6.0	35	17	787	31	4%	17	561	67	12%
2.5	1.0	45	17	284	56	20%	17	218	85	39%
2.5	1.0	35	17	501	65	13%	17	335	49	15%
3.5	1.0	35	17	497	77	15%	17	330	60	18%
3.5	1.0	45	17	247	57	23%	17	179	27	15%
3.5	6.0	35	17	666	95	14%	17	543	70	13%
3.5	6.0	45	17	597	72	12%	17	438	51	12%
3.0	3.5	40	17	599	73	12%	17	422	31	7%
3.0	3.5	40	17	599	92	15%	17	458	55	12%
3.0	3.5	40	17	567	149	26%	17	431	78	18%
				Average of 11 tests = 15%.				Average of 11 tests = 16%.		

TABLE III

Average corrosion rates and the standard deviations of SS 304

Conditions			48 hr test				120 hr test			
pH	Salt (%)	Temp (°C)	No. of sample	Avg. μm yr^{-1}	St dev μm yr^{-1}	Ratio (%)	No. of sample	Avg. μm yr^{-1}	St dev μm yr^{-1}	Ratio (%)
2.5	6.0	45	17	7	3	37%	17	5	1	26%
2.5	6.0	35	17	4	1	30%	17	3	1	21%
2.5	1.0	45	17	9	6	69%	17	6	2	34%
2.5	1.0	35	17	9	4	43%	17	6	3	52%
3.5	1.0	35	17	3	2	50%	17	2	1	41%
3.5	1.0	45	17	4	2	51%	17	2	1	45%
3.5	6.0	35	17	5	2	50%	17	2	1	34%
3.5	6.0	45	17	7	3	43%	17	4	2	35%
3.0	3.5	40	17	6	2	41%	17	3	1	18%
3.0	3.5	40	17	3	1	35%	17	2	1	36%
3.0	3.5	40	17	6	2	34%	17	2	1	22%
				Average of 11 tests = 44%.				Average of 11 tests = 33%.		

steel and aluminum, to 35% for SS 304. SS 304 had little corrosion even at the most severe condition, and thus had very small weight losses (less than 0.0005 g throughout the test in most of the specimens). Small errors in weight measurement could result in the poor reproducibility of SS 304. On the other hand, mild steel had the highest corrosion rate of the five tested metals and had also the highest reproducibility.

TABLE IV
Average corrosion rates and the standard deviations of red brass

Conditions			48 hr test				120 hr test			
pH	Salt (%)	Temp (°C)	No. of sample	Avg. μm yr^{-1}	St dev μm yr^{-1}	Ratio (%)	No. of sample	Avg. μm yr^{-1}	St dev μm yr^{-1}	Ratio (%)
2.5	6.0	45	17	179	15	8%	16	138	11	8%
2.5	6.0	35	17	158	19	12%	17	104	8	8%
2.5	1.0	45	17	179	18	10%	17	131	19	15%
2.5	1.0	35	17	143	25	17%	17	83	12	14%
3.5	1.0	35	17	130	14	10%	17	97	15	15%
3.5	1.0	45	17	167	14	8%	17	120	15	13%
3.5	6.0	35	17	123	8	6%	17	98	5	5%
3.5	6.0	45	17	165	17	10%	17	109	10	9%
3.0	3.5	40	17	160	10	6%	17	106	6	5%
3.0	3.5	40	17	155	14	9%	17	99	7	7%
3.0	3.5	40	17	153	12	8%	17	103	6	6%
				Average of 11 tests =		10%.		Average of 11 tests =		9%.

TABLE V
Average corrosion rates and the standard deviation of aluminum

Conditions			48 hr test				120 hr test			
pH	Salt (%)	Temp (°C)	No. of sample	Avg. μm yr^{-1}	St dev μm yr^{-1}	Ratio (%)	No. of sample	Avg. μm yr^{-1}	St dev μm yr^{-1}	Ratio (%)
2.5	6.0	45	5	41	4	9%	5	38	3	8%
2.5	6.0	35	5	30	6	20%	5	23	4	17%
2.5	1.0	45	5	86	40	47%	5	86	17	20%
2.5	1.0	35	5	40	8	21%	5	27	2	8%
3.5	1.0	35	5	21	5	26%	5	9	2	21%
3.5	1.0	45	5	34	10	28%	5	15	2	13%
3.5	6.0	35	5	30	2	7%	5	13	2	18%
3.5	6.0	45	5	30	5	16%	5	13	1	9%
3.0	3.5	40	5	44	6	13%	5	21	3	12%
3.0	3.5	40	5	31	5	16%	5	19	4	22%
3.0	3.5	40	5	45	5	11%	5	19	4	19%
				Average of 11 tests =		19%.		Average of 11 tests =		15%.

Three batches were conducted to check the reproducibility of corrosion rate measurements for all metals, except mild steel for which only two batches were conducted. They were conducted at the mid-level of each parameter, i.e. pH 3.0, 3.5% salinity and 40 °C. Comparison of the standard deviation to the average measurement of these reproducibility tests for each metal indicates that the batch reproducibility was satisfactory. Based on results of the 120 hr tests, the ratio of

standard deviation to the average measurement was 1% for mild steel, 3% for galvanized steel and red brass, 5% for aluminum, and 11% for SS 304.

Corrosion rate measurements

Comparison of the corrosion rates of different metals at the same condition, as shown in Tables I to V, indicates that there are order-of-magnitude differences. Using mild steel as reference, the ratios of corrosion rate at the nine test conditions between mild steel, galvanized steel, SS 304, red brass and aluminum were on the average about 1000 : 423 : 4 : 116 : 26.

At the conditions which simulated the acid rain/fog during summer in Hong Kong, i.e. pH 3.5, 1% salinty and 35 °C, the differences in corrosion rates were as obvious. The average corrosion rates based on 120 hr tests were 735, 330, 2, 97 and 9 $\mu m\ yr^{-1}$, respectively, for mild steel, galvanized steel, SS 304, red brass and aluminum. Using mild steel as reference, their ratios on the average were about 1000 : 449 : 3 : 132 : 12. For comparison, Wranglen (1985) reported that the ratios of corrosion rates in moist urban and industrial environment for mild steel, galvanized steel, copper and aluminum were 1000 : 100 : 5 : 5. The poor corrosion resistance for galvanized steel and red brass in this study could probably be attributed to the dezincification at high levels of chloride and sulfate.

For mild steel, there was little difference on the corrosion rate measured after 48 hr and those after 120 hr, suggesting that the corrosion rate is independent of duration. For the other four metals, however, the former was higher than the latter. It is probably due to the formation of a compact layer of rust on the metal surface. This layer could retard the diffusion of the fresh acid and salt to the inner unreacted metal. Thus, the corrosion rate decreases with time for these metals. The same phenomenon was reported for aluminum by McGeary *et al.* (1967). They found that during the first 1 or 2 yr, aluminum weathered rapidly in severe industrial or marine atmospheres. The rate of attack usually attenuates to fairly low values after this initial period.

Relative effects of 'acidity', salinity and temperature

Corrosion data of the 120 hr tests could be fitted satisfactorily in the following linear equation using regression analysis:

$$R = c_0 + c_1\,(7\text{-pH}) + c_2 S + c_3 T,$$

where R represents the corrosion rate ($\mu m\ yr^{-1}$), 7-pH the 'acidity', S the salinity (% of sodium chloride) and T the temperature (°C). Table VI summarizes the coefficients in the equation for each metal.

Using the coefficients in Table VI, the corrosion rate of each metal could be calculated. The accuracy of the calculated corrosion rates could be determined by comparing the average deviations of the calculated values against the measured values at the nine test conditions. Table VII shows the average ratio at all test conditions of the standard deviation of corrosion measurement for each metal.

TABLE VI

Coefficients of linear regression equations

	c_0	c_1	c_2	c_3
Mild steel	-851.2	350.3	20.4	8.5
Galvanized steel	343.0	65.5	58.3	-10.1
SS 304	-9.6	2.2	0.0	0.1
Red brass	-39.9	7.9	0.9	2.9
Aluminum	-167.7	30.8	-2.4	2.0

TABLE VII

Accuracies[a] of calculated corrosion rates from linear regression equation as compared with measurement errors

	Calculated accuracy (%)	Measurement error (%)
Mild steel	7	4
Galvanized steel	18	16
SS 304	36	33
Red brass	6	9
Aluminum	65	15

[a] Accuracy is expressed as the average ratio of (calculated – measured)/measured at the nine test conditions.

Comparison between these two sets of values shows that the linear regression equation gives reasonable estimates of corrosion rates. The accuracies of the calculated values from the equation were about the same as the measurment errors, except for aluminum. The average ratio and the standard deviations of measured values were 7 and 4% for mild steel, 18 and 16% for galvanized steel, 36 and 33% for SS 304, and 6 and 9% for red brass. However, for aluminum, the regression equation fails to give satisfactory estimation of corrosion rates; the average ratio was 65%, as compared to measurement error of 15%.

It is often tempting to apply regression equations to conditions outside the test ranges. Such an attempt is discouraged because the estimated results are unsatisfactory most of the time. Therefore, one should know the limitation and the risk if the regression equation is used to estimate the corrosion rates of the construction metals at milder conditions.

However, in the linear regression equation, the effect of each parameter to the corrosion rate is independent of other parameters. The corrosion rate, thus, is the summation of the three independent effects from 'acidity', salinity and temperature, plus a constant term. The magnitude of coefficients, c_1, c_2 and c_3, in Table VI shows the susceptibility of corrosion rate on 'acidity', salinity and temperature of the tested metals. All but one of the coefficients for mild steel, galvanized steel,

SS 304, and red brass are positive. This indicates that, within the test ranges, the corrosion rate of these metals appears to increase linearly with 'acidity', salinity and temperature. The only exception is galvanized steel, whose corrosion rate decreases as temperature increases, as shown by the negative sign of c_3. For comparison, it was reported by Stanners (1970) that the corrosion rate of Zn is insusceptible to temperature.

The small values of its coefficients show that SS 304 is least susceptible to all the parameters; it has little or no effect on the change of salinity and temperature, but has only small effect on the pH. Red brass is more susceptible than SS 304, but its susceptibilities to pH and salinity are one order of magnitude lower than those of mild steel and galvanized steel. Mild steel is about five times more susceptible to pH than galvanized steel. On the other hand, galvanized steel is about three times more susceptible to salinity than the former, probably due to the susceptibility of Zn to chloride attack.

Data in Table V show that corrosion rate of aluminum consistently increases as pH decreases; this is also reflected by the coefficient c_1. At pH 3.5, its corrosion rate was less than 15 $\mu m\ yr^{-1}$ for all tested salinity and temperature; at pH 2.5, it increased from 23 $\mu m\ yr^{-1}$, at 6% salinity and 35 °C, to 86 $\mu m\ yr^{-1}$, at 1% salinity and 45 °C. Since the corrosion rate data of aluminum could not be satisfactorily fitted by the linear regression equation, the effects of salinity and temperature are inconclusive.

Attempt was made to express the corrosion rate data by quadratic equations using multiple regression analysis. These more complex quadratic equations, however, gave little improvement on the accuracy of estimated rates for all the tested metals, including aluminum.

4. Conclusion

Corrosion of five most common construction metals were tested at nine conditions within the ranges of pH 2.5 to 3.5, salinity 1 to 6%, and temperature 35 to 45 °C. The average corrosion rates at the condition which simulated the acid rain/fog during summer in Hong Kong, i.e. pH 3.5, 1% salinity and 35 °C, were 735, 330, 2, 97 and 9 $\mu m\ yr^{-1}$, respectively, for mild steel, galvanized steel, SS 304, red brass and aluminum.

Corrosion rates of mild steel, galvanized steel, SS 304 and red brass could be satisfactorily fitted with linear regression equations. For these metals, the corrosion rate appears to increase linearly with the increase of 'acidity', salinity and temperature. The only exception is that galvanized steel's corrosion rate decreases as temperature increase.

The susceptibility to corrosion of each metal to the change of pH, salinity and temperature could be determined by the magnitude of the coefficients. Corrosion rate of SS 304 is least susceptible to the environment; it has little or no effect on the change of salinity and temperature, but has only slight effect on the pH.

Red brass is more susceptible than SS 304, but its susceptibilities to pH and salinity are one order of magnitude lower than those of mild steel and galvanized steel. Mild steel is about five times more susceptible to pH than galvanized steel; whereas the latter is about three times more susceptible to salinity than the former, due to the chloride attack of Zn.

Aluminum's corrosion rate increases as pH decreases; however, the effects of salinity and temperature are inconclusive.

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