Journal of Environmental Sciences (China), Vol. 3, No. 2, pp. 53–60, 1991 ISSN 1001–0742

Influence of acid deposition on atmospheric corrosion of zinc

Zheng Yiping[1], Wang Zhenyao[1] and Zhang Fengqiu[1]

(Received May 30, 1989)

Abstract—Site exposure tests both open and sheltered have been carried out in acid deposition area in Southwest China. Results from six sites show that acid deposition exerts a great influence on atmospheric corrosion of Zn, and it is more serious in wet condition. Basically, Zn corrosion is directly proportional to time of exposure. While SO_2 is the main pollutant of the atmosphere environment, Zn corrosion has a linear relationship to SO_2 depositing rate and a hyperbolic to rain pH value.

Observations by SEM, EDAX and X-ray diffraction show that under sheltered exposure condition, the corrosion products of Zn in heavy acid deposition area principally are sulphates.

Based on the corrosion rates measured, the working life of galvanized steel can be predicated.

Keywords: acid deposition; atmospheric corrosion; zinc.

INTRODUCTION

With the growing of modern industry and increasing consuming fuels(especially coal), problems of environmental pollution are getting more and more serious. Resulting in corrosion of materials much more attention has been taken. Systematic studies have been carried on in North Europe and North America (Baboian, 1986; Flinn, 1985). For the geological and environmental reasons in South China, especially in Southwest area, the problem of acid deposition is getting severe. In charge of studies of acid deposition in these areas and related problems of materials corrosion, some research group have been organized and supported by the government.

As a structural and coating material, zinc is widely used in architectures and industry. So studies of corrosion behaviour of Zn in different atmospheric pollution environments are of great practical and economical importance.

[1]Institute of Corrosion and Protection of Metals, Academia Sinica, Shenyang 110015, China.

EXPERIMENTAL METHOD

Choice of appropriate exposure site

Taking the difference of atmospheric pollution between regions into account, we take Chongqing City and Guiyang City as the heavy acid deposited areas, Chengdu City, Dazu County and suburban Leizhuang as the light acid deposited areas, and a clean area in Huitong County as background. The environmental parameters are listed in Table 1.

Table 1 Environmental parameters of exposure sites (1987.10– 1989.10)

Sites	Guiyang	Chongqing	Leizhuang	Dazu	Chengdu	Huitong
pH of rain	3.96	4.16	4.32	4.43	5.17	6.0
SO_2, $mg/m^2.d$	233	154	63.1	21.6	44	5.6

Exposure type

Using polycarbonate roof to shed rain but keeping sunshine and air circulation the same, both open and sheltered exposures are tested. According to ISO-4542 Standard, facing south and at 45° with the horizon, specimens are insulated with aluminum alloy frame by ceramic clamps.

Specimen preparation

The specimens are made from pure Zn and the contents of impurities are listed in Table 2.

Table 2 Impurities of zinc

Elements	Fe	Cu	Pb	Sn	Ca
wt, %	0.012	0.0005	0.040	0.0005	0.0005

Specimens, sized $100\times50\times2mm^3$ are polished by 500* sand–paper, then degreased and weighted.

After a time of exposure, the specimens are taken off the frame. 15% ammonium-hydroxide is used to wash corrosion products off surfaces, then the weight losses as a measure of corrosion rates are determined. Data are taken from mean value of three specimens.

EXPERIMENTAL RESULTS

Outlook

After exposure, specimen surfaces usually look grey or dark grey, samples from heavy acid deposition area sites, exposed under sheltered condition gave some visible white products on them.

Corrosion rates

The open exposure corrosion rates at each sites (Table 3) and their relative corrosion rates (Fig.1) are given.

Table 3 Corrosion rates of open exposures

Sites	Corrosion rate, μm/a	
	1st year	2nd year
Guiyang	5.8	5.7
Chongqing	4.5	5.4
Leizhuang	2.5	2.3
Dazu	2.1	1.8
Chengdu	1.5	1.4
Huitong	1.6	1.1

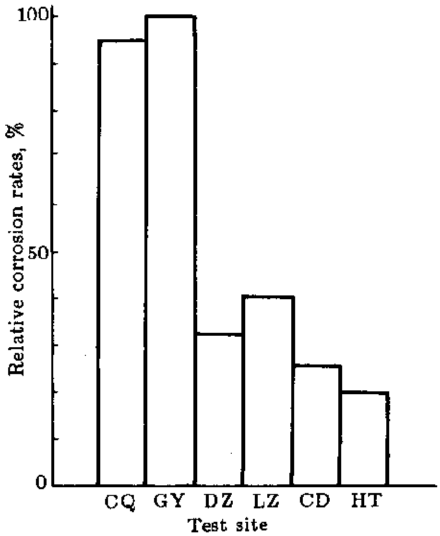

Fig. 1 Relative corrosion rates (1987.10–1989.10)

The ratio of maximum value (in Guiyang) and minimum (in Huitong) is 5.2, it indicates that substantial differences in corrosivity of the atmosphere exist. According to ISO/DP 9223 Standard submitted by ISO/TC 156 in 1986, by first year material corrosion rate data, Guiyang and Chongqing should be classified as C5, while Huitong as C2.

Comparison of open and sheltered exposure corrosion

To partition the effects of dry and wet acid deposition on zinc corrosion, two types of exposure have been carried out at Guiyang, Chongqing and Chengdu (Fig.2).

Weight losses has fairly direct relation with time under two types of exposure, that is, corrosion rate is constant and corroded layer is nonprotective. At same time, no matter where it is, corrosion rates under open condition are much greater than sheltered. Also because of differences in the degree of pollution the ratio of two rates varies from place to place. In seriously

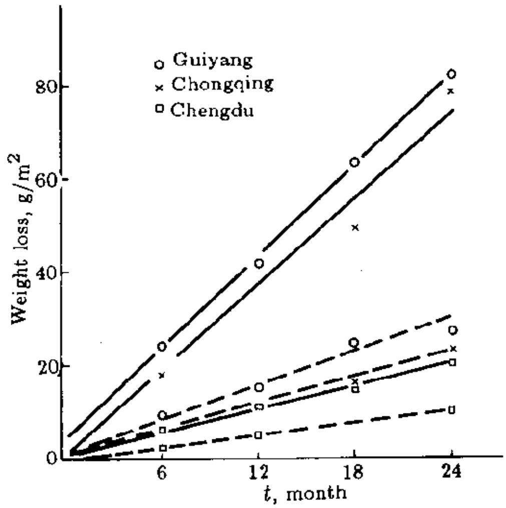

Fig.2 Corrosion rates in three exposure sites

(— open - - - sheltered)

polluted area as Guiyang and Chongqing it is 3, for light polluted Chengdu, it just takes 2.

Influence of SO_2 deposition rate on zinc corrosion

By exposing K_2CO_3 treated glass-fibre filter in air to capture SO_2, the SO_2 deposition rate can be determined (The Environmental Protection Agency of China, 1986). It can be seen that zinc corrosion is proportional to SO_2 deposition rate of the very exposure sites (Fig.3). Through linear regression analysis, correlation coefficients for the first and second years exposure are 0.98 and 0.96 respectively. Their correlation functions are as follows:

$$1 \text{ year}: K_1 = 9.55 + 0.134\ SO_2 \quad r = 0.96;$$

$$2 \text{ year}: K_2 = 14.2 + 0.317\ SO_2 \quad r = 0.94.$$

where K =weight loss (g/m^2), SO_2=deposition rate ($mg/m^2.d$) and r =correlation coefficient.

Influence of pH value of rain on zinc corrosion

pH value of acid rain has direct influence on zinc corrosion. The data measured show a hyperbolic relationship (Fig.4).

Simulative tests using dip-wet-cycle in the laboratory also give similar results (Fig.5). It is evident that corrosion rate goes up sharply when pH value is lower than 4.5 in the sites tests (Fig.4). But in laboratory pH value should be lower than 3.7 (Fig.5). As under site condition, other than the pH value of rain, some other factors will influence the corrosion as well. Furthermore, the pH values of rain fluctuate, the data taken are just the mean value of measurements.

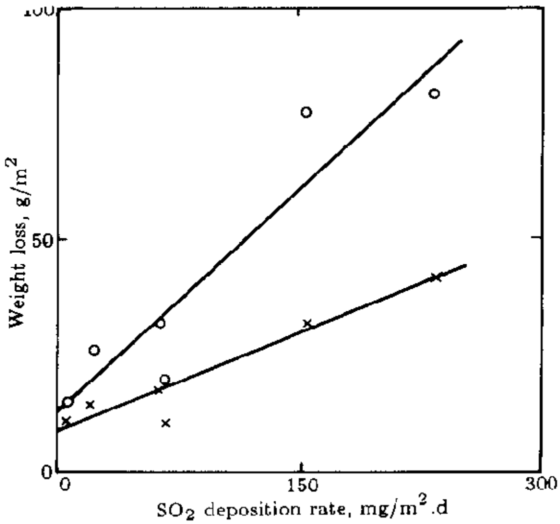

Fig.3 Effect of SO_2 deposition rate on corrosion
(x: 1 year; o: 2 years)

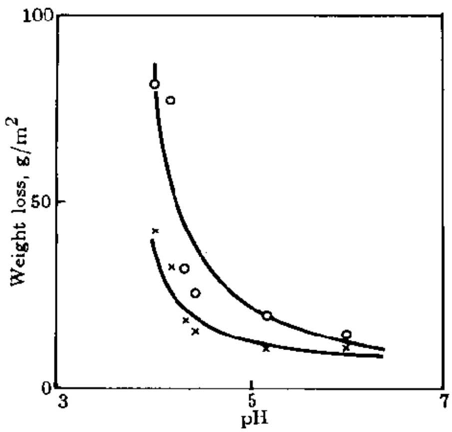

Fig.4 Effect of pH value of rain on corrosion
(x: 1 year; o: 2 years)

Characterization of the corrosion products

The corrosion products of zinc specimen surface from Chongqing site (open and sheltered) have been analyzed by SEM and EDAX. White and dark grey block structures and white needle-shaped structure have been found. Under sheltered condition, the content of sulfur in white needle-shaped structure will be up to 19 wt%, and it contains silicon, aluminum, iron and calcium from air-borne dust as well. Under open exposure condition, the content of sulfur is about 5 wt% (Fig.6, Table 4).

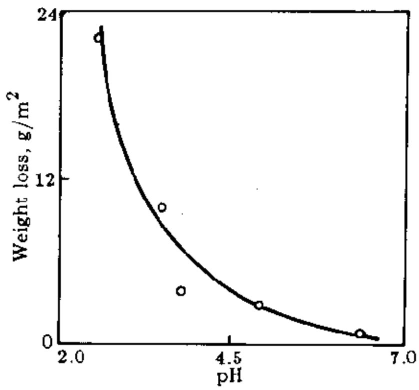

Fig.5 Effect of pH value of test solution on corrosion

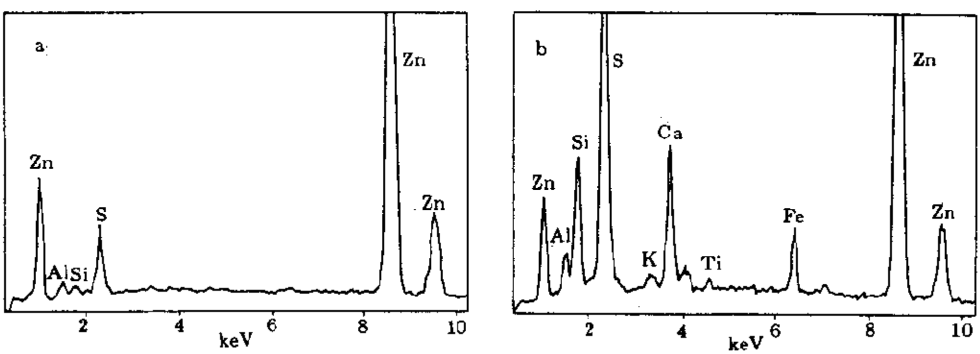

Fig.6 EDAX results of corrosion products

a: open exposure b: sheltered exposure

Table 4 EDAX analysis of corrosion products, wt%

Exposure type	Al	Si	S	K	Fe	Zn	Ca	Ti
Open	1.97	2.33	5.44	0.24	0.6	89.42	/	/
Sheltered	5.21	8.44	19.20	0.56	4.47	58.4	4.47	0.56

X-ray diffraction inspections show that, on the surface of specimens after 6 months sheltered exposure, there are products of $ZnSO_4.X\ H_2O$ on both skyward and groundward sides (Fig.7).

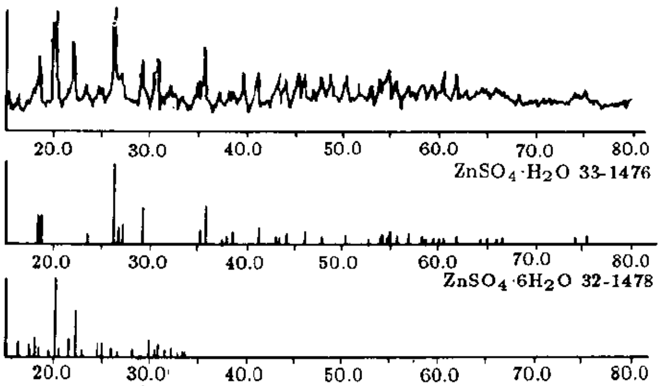

Fig.7 X-ray diffraction patterns of corrosion products

After two years exposure, the corrosion products of specimens at all sites are separated by ammonium hydroxide solution. By measuring sulfate ion contents of the solutions, relationship between zinc corrosion and sulfate ion contents is obtained (Fig.8) approximately, they are exponential curves.

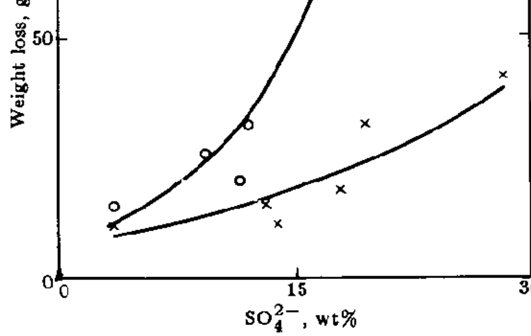

Fig.8 Relationship of corrosion and amount of sulfate ion in products

(x: 1 year; o: 2 years)

DISCUSSIONS

X-ray diffraction data show that the corrosion product is mainly composed of sulfates of zinc. Analyzing by energy dispersive X-ray analysis, besides dust and common elements in the soil, for the sheltered exposure specimens, the surface corrosion products contain sulfur and zinc, and the ratio of zinc and sulfur is similar to that of $ZnSO_4$. The $ZnSO_4$ is water soluble, which will be dissolved and washed away by rain, so there is much less corrosion product on open exposure specimen. As the main component of corrosion product, $ZnSO_4$ must be produced by the action of SO_2 oxidized into SO_3 in air. That is the reason why the degree of zinc corrosion will linearly related to SO_2 content in air. The poor combination between zinc and zinc sulfate produced on specimen surface can not protect the surface from air. So that the corrosion rate will not change with exposure time. The fact shows that one can evaluate the working life of members reliably by measuring the year rate of zinc corrosion.

Oxides of sulfur in air will dissolve in rain water and change its pH value. It is obvious that the pH value of 4.5 is an important turning point to zinc corrosion. When pH is lower than 4.5, the zinc corrosion rate goes up sharply. In general, thickness of zinc coating is usually about 20μm. The yearly corrosion rate of zinc is 4–6μm in Chongqing and Guiyang, therefore their working life will not be more than four years. It is evident that to control the air pollution and decrease the acid deposition is an urgent problem in economical construction.

Acknowledgements— We thank to the cooperation of Sichuan, Guizhou and Chongqing Institutes of Environmental Protection in measurement of environmental parameters.

REFERENCES

Baboian, R., ACS Symposium Series, 318, ACS, Washington, DC, 1986

Flinn, D.R., Cramer, S.D., Carter, J.P. and Spence, J.W., Durability of Building Materials, 1985, 3:147

The Environmental Protection Agency of China, Method of environmental monitor analysis, China Environmental Science Press, 1986:198