钢铁材料
腐蚀与控制技术

Corrosion and its Control of Iron & Steel

韩 冰 杨朝晖 曲 政 等编著

中国海洋大学出版社

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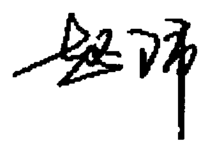
序

走进钢铁研究总院青岛海洋腐蚀研究所的大门，给我的视野开阔，心旷神怡.一边是绿色，一边是蓝色，美景尽收眼底.在那翠绿挺拔的龙柏丛中，点缀有马尾松、海藤树以及依地势而建的错落有致的办公楼和试验场地.站到古色古香的“望景亭”中，远眺着一望无际的蓝色大海，与天相连.隔海相望，披绿的浮山脚下层层叠叠的别墅群和居住小区，呈现出青岛“红瓦绿树、碧海蓝天”的城市美景.我十分羡慕在此美景下工作的同事.

钢铁研究总院青岛海洋腐蚀研究所取得的成就可与美景媲美.青岛海洋腐蚀研究所自1972年选址筹建，1975年正式挂牌.30多年来，该所一直承担着国家科技部、自然科学基金委、国防科工委的重大研究课题，积极参与国家重大工程项目，开发出一批拥有自主知识产权的专有技术，广泛应用于国防军工、海洋工程、石化、电力、冶金、家用电器等领域.该所是国家水环境腐蚀网站示范站和组长单位、大气腐蚀网站重点站，培养出了一批年轻优秀的复合型人才队伍，成为国内从事金属材料腐蚀与防护领域应用研究的一支重要力量.

此次，《钢铁材料腐蚀与控制技术》一书的出版问世，汇集了该所在金属腐蚀和防护领域最近十年的部分研究成果，包括自然环境中钢铁材料的腐蚀等方面的技术数据和实践经验，涉及面广、实用性强，有助于读者了解金属材料腐蚀与防护领域的研究现状、重要技术及其在工程上的应用以及与先进国家的差距.它的出版，一定会对我国从事金属材料的腐蚀与防护的科研、工程技术和管理等有关人员起到积极的借鉴作用.



2006年8月8日

前言

钢铁研究总院青岛海洋腐蚀研究所是钢铁研究总院设在青岛的直属研究单位.该所自1975年成立以来,历经科技人员的努力奋斗,现已具有承担重大金属腐蚀与防护技术的研究和工程设计、施工的能力,是国家水环境腐蚀网站示范站和组长单位、大气腐蚀网站重点站,一直承担国家科技部和自然科学基金委重大项目"材料在我国自然环境中的腐蚀数据积累及规律性研究"的相关课题,建有中国海水腐蚀、大气腐蚀数据库,取得了丰硕的研究成果.研发的防腐蚀技术与产品已广泛应用于海洋工程、埋地管线、家用电器以及石化、电力、冶金、市政等领域,取得了显著的经济效益和社会效益,为国民经济建设作出了贡献.

本书是钢铁研究总院青岛海洋腐蚀研究所建所以来,尤其是近十年工作的总结,它汇集了编著者们在国内外各类刊物、学术会议发表的部分论文.编著者都是从事金属腐蚀与防护技术研究和工程设计、实施的科技人员.他们通过大量的腐蚀试验研究以及防护技术的实施应用,积累了详实、丰富的技术数据和经验,本书是他们聪明才智的结晶.

钢铁研究总院院长、中国工程院院士干勇专门为《钢铁材料腐蚀与控制技术》一书题词——"积青岛所卅年技术底蕴,发展钢铁材料海洋防腐事业",钢铁研究总院副院长赵沛亲自为本书作序,在此表示衷心感谢.

本书在编写过程中,得到了朱相荣、侯文泰、周来金、张晶等同志的协助与帮助.在此一并表示感谢!

限于水平,本书的缺点和不足在所难免,恳请读者批评指正.

编著者

2006年8月

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第一篇　自然环境中钢铁材料的腐蚀

一、大气腐蚀

Atmospheric Corrosion Prediction of Steels

ABSTRACT The atmospheric corrosion data of steels after sixteen-year exposure at various sites in China were obtained, and power function was used for regression of the corrosion mass loss. Parameters of the power function derived from these exposure data were used as the variants for a multi-argument linear stepwise regression, which was utilized to analyze the effects of various factors on the corrosion. Both chemical compositions of steels and the environment factors were used as the arguments in the step regression. Quantitative relation of the corrosion parameters with both environment factors and chemical compositions of steels was obtained. As a result, corrosion can be predicted for most carbon and low alloy steels in a variety of environments.

KEY WORDS atmospheric corrosion, steel, corrosiveness, prediction

1 INTRODUCTION

For their excellent mechanical properties and relatively low price, carbon steels and low alloy steels have become the main materials for structures in atmosphere. To improve their corrosion resistance, atmospheric corrosion of steels has become one of the main study subjects since the beginning of the 20th century. Great efforts have been made in the past thirty years to get quantitative estimation or prediction of atmospheric corrosion of steels in terms of the chemical compositions of the steels and the environment factors.

Quantitative relation between corrosion weight loss and the compositions of steels was obtained by Legault and Leckie[1] in 1974 from the data of 273 steels exposed at 3 sites for 15. 5 years by Larrabee and Coburn[2]. In their study, stepwise multiple regressions were used in obtaining the equation, and based on this equation a standard guide was made by ASTM for estimating the atmospheric corrosion resistance[3].

Quantitative relation between atmospheric corrosion of steels and environment factors was pursued by Feliu *et al* in 1993[4], Rosales *et al* in 1996[5] and Mendoza *et al*[6] in 1999, respectively. ISO-DIS9223 standard[7] stipulated to determine corrosiveness of three environment factors — humidity hours, sulphur dioxide pollution and sodium chloride pollution. It also stipulated to determine corrosiveness by one-year exposure data of carbon steels.

All the works mentioned above took corrosion weight loss as the corrosion parameter in their regressions. Their results can be used for comparison of the corrosion resistance of steels or the corrosiveness of environments. This is helpful in the production of steels with better atmospheric corrosion resistance or in preventing us from using low atmospheric corrosion resistant steel for outdoor structures. However, these results cannot be used for corrosion predictions. Studies have shown that atmospheric corrosion development in long-term exposure is completely different from that in short-term corrosion exposure. This phenomenon is demonstrated by Fig. 1, which shows the corrosion curves of a mild steel exposed at seven different sites.[8] If the corrosiveness of the steel was determined by the corrosion of one-year exposure, according to ISO9223, Wanning will be one of the least corrosive sites. To the contrary, it is the most corrosive one after four-year exposure. Therefore, it is not appropriate to compare the corrosiveness of steels by corrosion weight loss in a fixed period, not to say by one-year exposure weight loss data.

Many studies have shown that the development of atmospheric corrosion of steels follows the widely used power function:

$$D=At^n. \qquad (1)$$

In which, D is the corrosion depth in mm, t is the exposure time in years, and A and n are two parameters.

Fig. 1 and 2 show the good agreement of the corrosion data with the power function regression curves[8]. Corrosion behaviors can be predicted if the parameters A and n of the power function are determined.

A different quantitative relation between corrosion and the chemical compositions of steels was obtained by Liang and Hou[9] in 1995. Parameters of the power function, which were derived from the corrosion weight loss of steels exposed for 8 years at different sites, were used for the regression. Corrosion can be predicted by this relation for steels in typical environments as far as the chemical compositions of the steel are given. In 2001, Townsend[10] used similar method and obtained quantitative equations for steels in industrial environment. These methods are a big step forward for corrosion resistance determination of steels. It allows us to predict the corrosion behavior of a steel in certain environment. However, the words "typical", "industrial", "rural" and "marine" for environment are quite ambiguous. It will be a breakthrough, if in addition to chemical compositions, environment factors are also taken into consideration in the regression equation. Then theoretically it will be possible to predict corrosion for any steel in any environments.

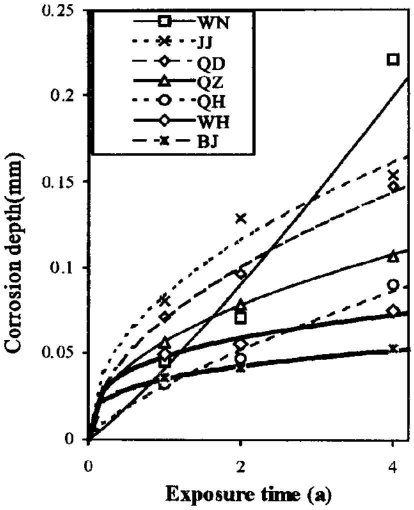

Fig. 1 Atmospheric corrosion of a mild steel at seven different exposure sites (the symbols indicate the actual data, and the lines are the power function regression curves)

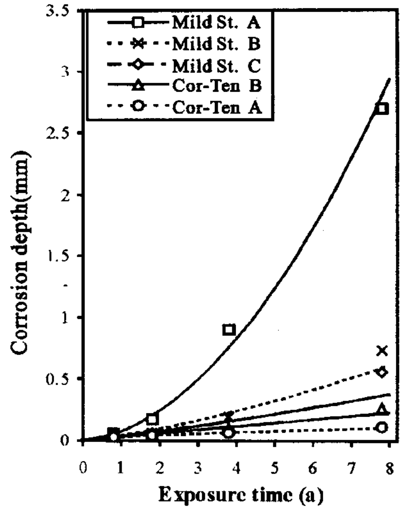

Fig. 2 Atmospheric corrosion of various steels at Wanning, China (the symbols indicate the actual data, and the lines are the power function regression curves)

In this paper, stepwise regression program was used to our data of steels after sixteen-year exposure at various sites in China for the analysis of the effects of different factors on the atmospheric corrosion of steels. A quantitative relation of corrosion with both environment factors and chemical compositions of steels was obtained. And corrosion can be predicted by this relation for low carbon and alloy steels in certain environments as far as the chemical compositions of the steels and the environment factors are given.

2 EXPOSURE TESTS AND RESULTS

Seventeen industrially manufactured steels were exposed since October 20, 1984 for sixteen years at typical exposure sites in China. The details of the exposure and the corrosion data of 4-year and 8-year exposure have been published previously 8. Here only the chemical compositions of the tested steels and the environment data at the exposure sites are listed in Table 1 and Table 2.

Weight loss of the steel coupons at six different sites after sixteen-year exposure was obtained in this study. Both 8-year and 16-year exposure data showed that the widely used power function, i. e. equation (1), was still the best to describe the corrosion process. The results of the power function regression using the 16-year corrosion data are listed in Table 3 and Table 4. (Low corrosion resistant steels coupons were perforated and collapsed after 16-year exposure at Wanning, the most corrosive exposure site.

Also, some coupons were lost at some other sites. Therefore, some data were missing in Table 3 and 4.)

Fig. 3 shows the corrosion of steel 14 (a typical mild steel) at different exposure sites. Fig. 4 shows the corrosion of various steels at Wanning, the most corrosive one among the six sites.

Table 1 Chemical compositions of the tested steels(%)

Steel	C	S	P	Mn	Si	Cr	Ni	Mo	Cu	Nb	V	Ti	Al	RE	N	B
1	0.07	0.023	0.090	0.4	0.5	0.4	0.6	0.06	0.38							
2	0.08	0.023	0.070	0.4	0.5	0.6	0.3		0.41							
3	0.11	0.019	0.080	0.4	0.3		0.4		0.27							
4	0.08	0.019	0.089	0.4	0.3				0.29			0.01		0.01		
5	0.10	0.002	0.010	0.3	0.6	0.8		0.1	0.25		0.05					
6	0.09	0.002	0.012	0.5	0.4	1.0		0.3	0.09					0.57		
7	0.15	0.010	0.022	1.5	0.3			0.6		0.04						0.004
8	0.19	0.004	0.026	1.5	0.4			0.5			0.15				0.01	
9	0.13	0.022	0.011	0.8	0.3	0.6			0.20							
10	0.14	0.018	0.022	1.4	0.4				0.05	0.03						
11	0.17	0.023	0.030	1.4	0.3				0.07							
12	0.20	0.009	0.015	0.6	0.3											
13	0.14	0.027	0.035	0.9	0.4				0.08							
14	0.25	0.027	0.013	0.5	0.3	0.4										
15	0.10	0.024	0.027	1.2	0.2					0.03						
16	0.16	0.025	0.009	1.4	0.4											
17	0.08	0.025	0.008	0.4	0.1									0.05		

Table 2 Environment factors of the exposure sites**

		BJ	QD	JJ	GZ	QH	WN
Temperature (Average)	(℃)	12	12.5	18.4	22.4	24.5	24.6
Humidity (Average)	(%)	57	71	81	78	86	86
Humidity over 80% Hrs	(Hrs/a)	2 358	4 049	5 304	5 048	6 314	6 736
Precipitation	(mm/a)	552	643	939	1 494	1 881	1 563
Sun shine Hrs	(Hrs/a)	2 150	2 078	1 312	1 636	2 116	2 043
Cl^- Deposition	[mg/(100 cm² · d)]	0.049	0.25	0.006	0.024	0.199	0.387
SO_2 Deposition	[mg/(100 cm² · d)]	0.442	0.494	0.667	0.107	0.15	0.06
NO_2 Content	(mg/m³)	0.022	0.038	0.007	0.035	0.008	0.005
H_2S Content	(mg/m³)	0	0.013	0.004	0.007	0.029	0
Rain pH		5.5	6.1	4.4	5.8	6.9	5
Cl^- Content in rain	(mg/m³)		11 044	1 994	353	1 873	11 229
SO_4^{2-} Content in rain	(mg/m³)		81 654	31 642	13 702	9 625	3 552
Distance to sea	(m)		34				350

** Remarks: BJ—Beijing, QD—Qingdao, JJ—Jiangjin, GZ—Guangzhou, QH—Qionghai, WN—Wanning

Multiple stepwise regression program was used to analyze the effects of various factors on the corrosion of the steels. The parameters in the power function, A and n, were used as the variants in the stepwise regression. Environment factors and chemical compositions were used as the arguments in the program. A and n values in Table 3 and Table 4 were fitted to the following equations:

Table 3 Coefficient A obtained from 16-year exposure data

Steel	BJ	QD	JJ	GZ	QH	WN
1	0.030	0.057	0.074	0.056	0.022	—
2	0.030	0.055	0.062	0.053	0.023	—
3	0.033	0.065	0.086	0.054	0.026	0.035
4	0.035	0.109	0.133	0.068	—	—
5	0.032	0.055	0.083	0.059	0.023	—
6	0.029	0.051	0.061	0.046	0.022	0.025
7	0.030	0.051	0.062	0.053	0.021	0.022
8	0.028	0.045	—	0.045	0.019	0.021
9	0.032	0.047	0.066	0.048	0.021	0.021
10	0.029	0.057	0.069	0.052	0.022	—
11	0.027	0.050	0.054	0.041	0.019	—
12	0.031	0.047	0.059	0.048	0.019	0.023
13	0.027	0.048	0.053	0.044	0.020	0.021
14	0.032	0.050	0.065	0.055	0.023	0.033
15	0.027	0.047	0.056	0.042	0.021	0.025
16	0.022	0.049	0.054	0.044	0.020	0.033
17	0.032	0.047	0.053	0.042	0.019	0.028

Table 4 Coefficient n obtained from 16-year exposure data

Steels	BJ	QD	JJ	GZ	QH	WN
1	0.42	0.61	0.41	0.41	1.05	—
2	0.45	0.61	0.43	0.40	1.01	—
3	0.41	0.65	0.42	0.51	1.10	1.48
4	0.45	0.81	0.53	0.51	—	—
5	0.44	0.65	0.44	0.49	1.13	—
6	0.44	0.60	0.43	0.52	0.93	1.44
7	0.42	0.61	0.42	0.43	1.03	1.44
8	0.39	0.51	—	0.48	0.90	1.17
9	0.39	0.54	0.43	0.56	0.85	1.13
10	0.48	0.62	0.42	0.50	1.07	—
11	0.39	0.53	0.37	0.45	0.80	—
12	0.26	0.39	0.60	0.52	0.77	0.91
13	0.29	0.45	0.49	0.42	0.70	0.90
14	0.38	0.56	0.45	0.45	0.89	0.78
15	0.33	0.46	0.40	0.41	0.66	0.72
16	0.40	0.51	0.41	0.38	0.75	0.58
17	0.25	0.44	0.40	0.38	0.70	0.68

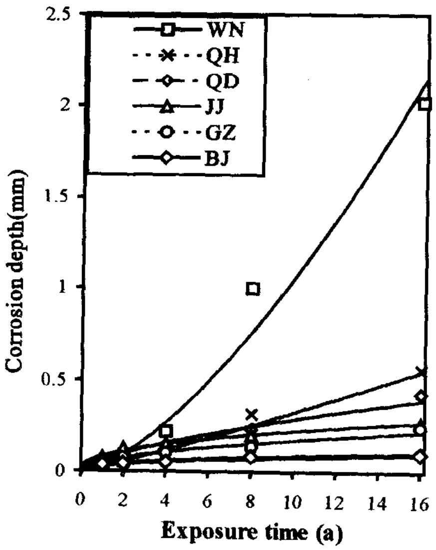

Fig. 3 Atmospheric corrosion of a mild steel after 16-year exposure at six different sites (the symbols indicate the actual data, and the lines are the regression curves)

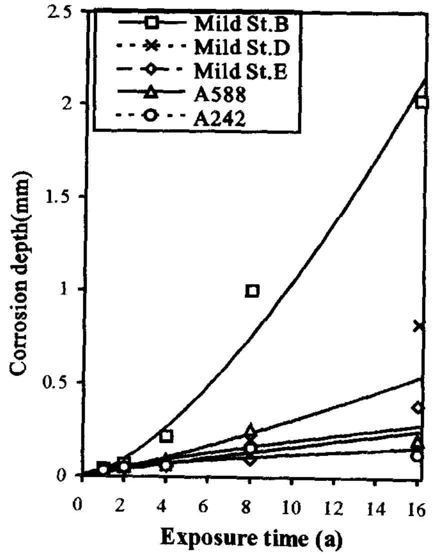

Fig. 4 Atmospheric corrosion of 5 different steels after 16-year exposure at Wanning, China (the symbols indicate the actual data, and the lines are the regression curves)

$$A = A(0) + \sum A(i)X(i) \tag{2}$$

$$n = n(0) + \sum n(i)X(i) \tag{3}$$

Here, $A(0)$ and $n(0)$ are constants, $A(i)$ and $n(i)$ are coefficients for factor i, and $X(i)$ is the quantity of the factor i. $X(i)$ is the concentration of the chemical elements of the steels when the factor is a chemical element of the steel, and $X(i)$ is the amount of the environmental factor if the factor i is an environment factor, such as temperature.

Various factors and their combinations were tried to be taken into the equation to make the error less. The best regression results so far are given in Table 5. The multi-relation coefficient value is 0. 82 for A and is 0. 90 for n.

The measurements of the arguments in the table have been adjusted, such that the adjustment put all the quantities of the arguments at the same order. This does not affect the regression results but make the comparison of the coefficients, i. e. the effect of various arguments, more visual.

The coefficients in table 5 were used to calculate the A and n values with Equation (2), (3) and then the 16-year corrosion depth with Equation (1) for the steels used in regression. The comparison of calculated and the actual corrosion depth after 16-year exposure at the six sites is given in Fig. 5, which shows a good correlation. Comparison was also made for the calculated and the actual corrosion depth after 1-, 2-, 4-, 8- and 16-year exposure at each site. The plots are given in Fig. 6-11. The correlation is very good for data obtained in Qingdao - the site with mild climate but with marine pollution, and in Qionghai - sub tropic site without much pollution. It is only not satisfactory for Beijing, the least corrosive site with mild and dry whether.

Table 5 Coefficients and constants for calculating *A* and *n* by environment factors and chemical compositions of steel

Stepwise regression result with the model of $A=A(0)+\sum A(i)X(i)$, $n=n(0)+\sum n(i)X(i)$

Arguments	Measurement	n	A(mm/a)	Remarks
Constant		−0.079	0.031	
Relative Humidity	(%)/100	0.216	——	Annual average
Temperature	(℃)/100	——	0.367	Annual average
Cl^-	[mg/(100 cm² · d)]	1.022	0.016	Deposition rate
SO_2	[mg/(100 cm² · d)]	0.195	0.028	Deposition rate
Precipitation * Sun shine hour	(mm/a) * (Hrs/a)/10^6	0.145	−0.021	Total of a year
Cu	(%)	−0.452	——	Content in steel
Mn	(%)	——	−0.013	Content in steel
Si	(%)	0.052	−0.022	Content in steel
P	(%) * 10	−0.069	−0.024	Content in steel
S	(%) * 10	0.375	0.036	Content in steel
Cr	(%)	−0.025	−0.012	Content in steel
Ni	(%)	——	——	Content in steel
Mo	(%)	——	——	Content in steel
C	(%)	——	——	Content in steel

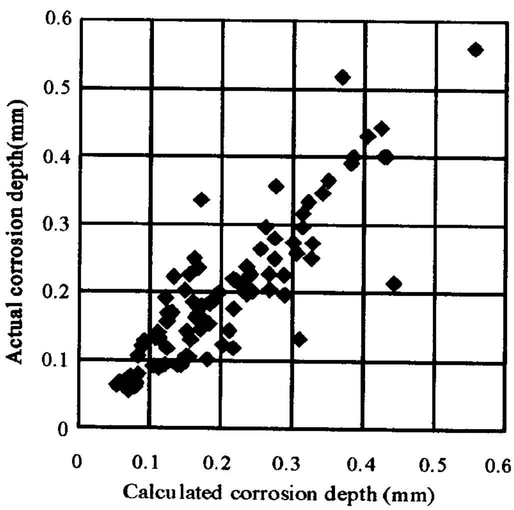

Fig. 5 Comparison of the calculated and the actual corrosion depths of 17 steels after 16-year exposure at 6 sites in China

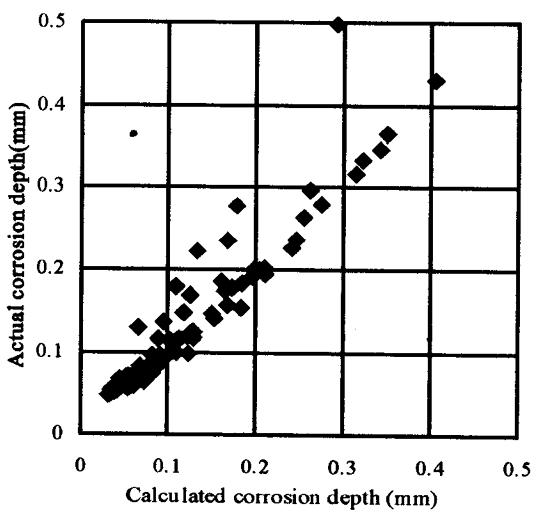

Fig. 6 Comparison of the calculated and the actual corrosion depths of 17 steels after 1-, 2-, 4-, 8-, 16-year exposure at Qingdao, China

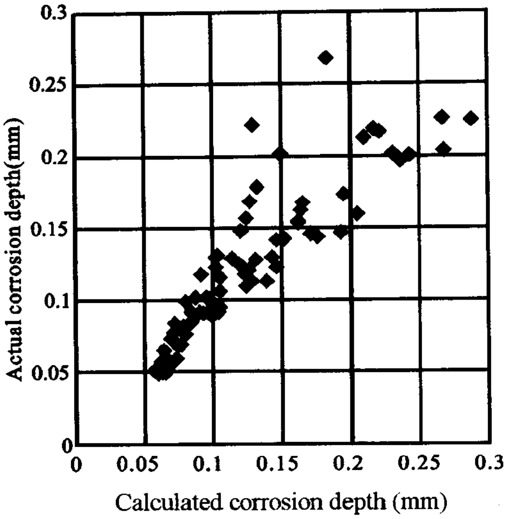

Fig. 7 Comparison of the calculated and the actual corrosion depths of 17 steels after 1-, 2-, 4-, 8-, 16-year exposure at Jiangjin, China

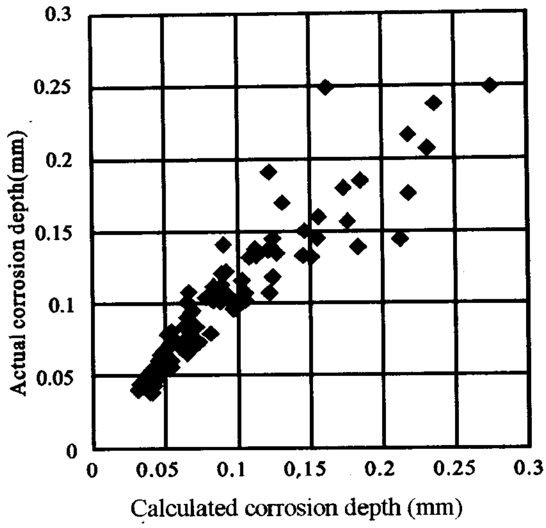

Fig. 8 Comparison of the calculated and the actual corrosion depths of 17 steels after 1-, 2-, 4-, 8-, 16-year exposure at Guangzhou, China

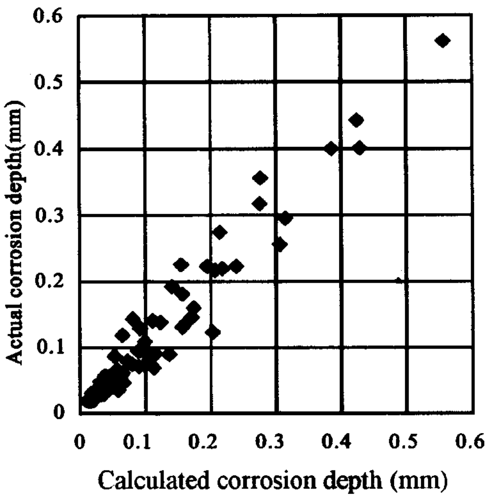

Fig. 9 Comparison of the calculated and the actual corrosion depths of 17 steels after 1-, 2-, 4-, 8-, 16-year exposure at Qionghai, China

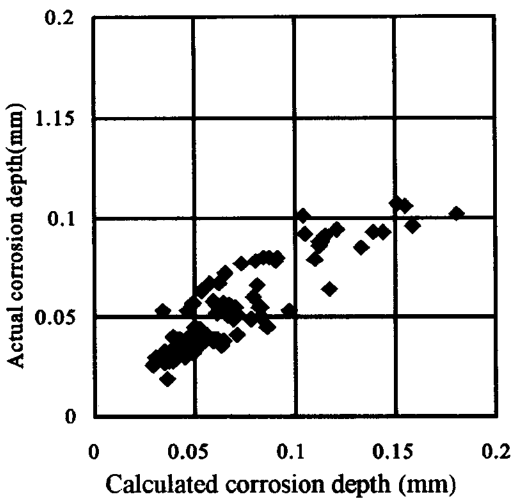

Fig. 10 Comparison of the calculated and the actual corrosion depths of 17 steels after 1-, 2-, 4-, 8-, 16-year exposure at Beijing, China