

## The Study on the Effects of Air Pollution on the Material Damages in Northeast Asia

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(Received 29 August 2002, accepted 12 April 2003)

### Abstract

The material exposure tests have been carried out since 1993 to evaluate the relationship between air pollution and material corrosion with the cooperation of the researchers in Japan, China, and Korea. The test pieces such as bronze, copper, marble, and carbon steel have been exposed under both unsheltered and rain-sheltered outdoor condition separately at 18 sampling sites in East Asia. At the same time, the concentration of SO<sub>2</sub> and NO<sub>2</sub> has been measured simultaneously with passive sampler. The meteorological data were collected from the AWS (Automated weather station) in each country and chemical compositions of wet deposition were also analyzed by the bulk sampling of rainfall every month. As the results, it was found that the corrosion rates of test pieces in the ambient air were appeared to be in the order of carbon steel > marble > bronze ≥ copper. The corrosion rates of test pieces in the unsheltered outdoor condition were 2.34 to 5.88 times larger than those in rain-sheltered condition. It was also found that the corrosion rate in the heavy polluted area in China was the highest, and the corrosion rates of the metal pieces were generally proportional to SO<sub>2</sub> concentration. Between two sites in Korea, the test pieces at Daegu site showed higher corrosion rates that would be due to the higher SO<sub>2</sub> concentration.

**Key words** : Air pollution, Material damage, Corrosion rate, Cultural properties, SO<sub>2</sub>, Northeast Asia

### 1. INTRODUCTION

It is evident that air pollution affects not only human health but also the material damage including the cultural properties. East Asian countries have very long cultural history, so we have a variety of cultural properties that have to be preserved for the following generations. However, recently the air pollution that is caused by the rapid industrialization and urbanization over the past decades in East Asia including China,

Japan, and Korea has resulted in the corrosion and damage of the cultural properties.

Cultural properties are composed of a variety of materials such as wood, paper, metal, stone and so on. Because of their special characteristics, collecting of samples that may involve their destruction cannot be permitted, even for cultural preservation activities. Except the human intentional destructions, the environment surrounding the cultural properties might be the most significant factor in considering their protection and preservation (Ninomiya *et al.*, 1997).

In Europe, there were some studies like as the cost evaluation of building damage by acidic deposition

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(David and Helen, 1996) and the impact assessment of gaseous  $\text{HNO}_3$  on the calcareous stones (Kirkitsov and Sikiotis, 1996) and so on. In Far East Asia, the Committee on the Cultural Properties and Materials Damage by Air Pollution has been initiated in June 1993 in order to evaluate the effects of acid deposition on cultural properties. This international project was organized by the Air Pollution Subcommittee of the Japan Society for Atmospheric Environment and funded by Global Environment Research Fund of the Japan Environment Agency (Maeda *et al.*, 2001).

In this paper, we are going to discuss the experimental results that have been performed to investigate the relationships between air pollution and material corrosion in East Asia during a last decade.

## 2. MATERIALS AND METHODS

The location of the sampling sites in East Asia is shown in Fig. 1. The sampling sites for our experiment were total 18 sites including 6 sites in China, 10 sites in Japan, and 2 sites in Korea. For our analysis' convenience, we classified these sampling sites into seven categories as presented in Table 1; the urban sites in

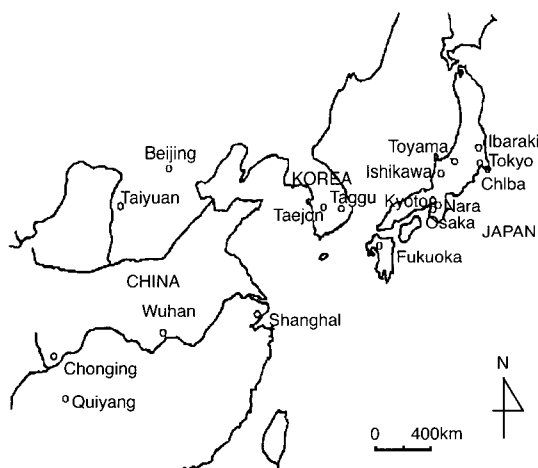


Fig. 1. The location of sampling sites for the materials exposure test.

Table 1. Classification of sampling sites in Northeast Asia.

Classification	Number	Sites		
Urban	3	Tokyo	Osaka 1	Osaka 2
Rural	4	Nara	Kyoto	Fukuoka Ibaraki
Sea coast	3	Ishikawa	Toyama	Chiba
China Heavy Polluted	3	Chongqing	Quiyang	Taiyuan
Urban	3	Beijing	Shanghai	Wuhan
Korea Suburb 1	1	Daegu		
Suburb 2	1	Daejeon		

Japan-Tokyo, Osaka 1, 2, the rural sites in Japan-Kyoto, Nara, Fukuoka and Ibaraki, and the sea coast sites in Japan-Ishikawa, Toyama, and Chiba, the heavy polluted sites in China-Chongqing, Quiyang and Taiyuan, the urban sites in China-Beijing, Shanghai and Wuhan, the two suburb sites in Korea-Daegu and Daejeon. Even though the specific information were not given in this paper, these classifications could be understood to be based on the characteristics of the geological location, urban scale, the level of air quality and so on.

For instance, Taiyuan, the capital of ShanXi in China, is a heavy industrial city; its main industry is coal, metallurgy, chemical industry, electric power and so on. The heavy industrial factory occupies 63% (1,295 factories), and main energy resource in this city is the mid-sulfur coal (XinWen, 1997). In addition, Chongqing district of south-western China, has been used the low-graded raw coal ( $S\% = \text{ca. } 2 \sim 6$ ) for the household heating and industrial purposes (Wang *et al.*, 1997).

The test pieces used in this experiment were bronze, ancient copper, pure copper, carbon steel and marble. Two sets of test pieces were exposed under both unsheltered and rain-sheltered outdoor conditions separately.

The exposed test pieces were collected every three months, a year, two years, and four years, and a variety of experiments were carried out related with the characteristics of corrosion products and damage patterns including the chamber experiment (Tsujino *et al.*, 2001). Among those experiments, we are going to report and discuss in this paper only about the one-year average of corrosion rates of test materials.

**Table 2. The physical properties of test pieces used in this study.**

Material	Size (mm)	Specific gravity (g/cm <sup>3</sup> )	Component
Bronze	2.0 × 30 × 40	8.9	JIS H 511 BC6 Cu 85%, Sn 5%, Pb 5%, Zn 5%
Ancient copper	0.8 × 30 × 40	8.9	Cu 99.28%, Pb 0.58%, As 0.02%, Zn 0.002%, Fe 0.001%
Copper	0.4 × 30 × 40	8.9	JIS H 3100 C1201P, Cu > 99.9%
Steel	1.2 × 30 × 40	7.9	JIS G 3141 SPPC
Marble	5.0 × 20 × 20	2.7	

**Table 3. The average value of the environmental factors in East Asia.**

Sites	Period	Temp (°C)	RH (%)	WV (m/s)	SO <sub>2</sub> (ppb)	NO <sub>2</sub> (ppb)	Rainfall (mm)	pH	SO <sub>4</sub> <sup>2-</sup> (μg/l)	NO <sub>3</sub> <sup>-</sup> (μg/l)	Cl <sup>-</sup> (μg/l)	NH <sub>4</sub> <sup>+</sup> (μg/l)	Ca <sup>2+</sup> (μg/l)	Mg <sup>2+</sup> (μg/l)	K <sup>+</sup> (μg/l)	Na <sup>+</sup> (μg/l)	
Japan	Tokyo	93.06.02 ~99.06.01	16.1	66.4	2.7	16.0	32.9	1526	6.1	1.5	1.1	1.2	0.4	3.4	0.2	0.0	0.4
	Osaka 1	93.06.01 ~99.06.01	17.2	65.7	2.2	6.4	33.1	1308	4.2	7.2	2.1	1.2	2.0	1.0	0.1	0.0	0.6
	Osaka 2	93.06.01 ~96.06.01	16.4	66.6	2.6	7.2	33.6	900	4.7	10.5	2.8	1.9	4.6	1.5	0.2	0.1	0.9
	Kyoto	93.06.02 ~99.06.01	15.6	76.0	1.4	4.3	18.8	1434	4.8	1.6	1.2	0.7	0.4	0.3	0.1	0.1	0.3
	Nara	93.06.01 ~99.06.01	16.5	68.0	1.8	4.8	20.2	1082	4.2	7.4	1.6	1.0	1.6	0.6	0.1	0.1	0.5
	Fukuoka	97.06.01 ~99.06.01	15.9	76.4	1.3	4.2	11.1	2131	4.8	1.9	0.9	1.3	0.5	0.2	0.1	0.1	0.6
	Ibaraki	94.06.01 ~99.06.01	14.0	73.4	2.2	3.6	11.9	1234	4.8	3.3	2.0	1.4	0.5	0.4	0.1	0.1	0.7
	Ishikawa	94.06.01 ~98.06.01	14.6	72.8	2.3	4.9	11.1	2522	4.2	4.9	1.5	5.6	0.4	0.4	0.4	0.2	3.3
	Toyama	97.06.12 ~99.06.01	13.9	79.7	1.8	3.1	12.7	2949	4.1	4.7	1.5	3.9	0.7	0.3	0.3	0.1	2.6
	Chiba	93.06.01 ~99.06.01	15.8	72.0	3.5	8.5	24.1	1366	-	3.6	1.9	3.0	0.7	1.7	0.3	0.2	1.9
China	Chongqing	93.06.04 ~00.06.01	18.4	80.4	1.4	101.2	21.1	1031	5.6	47.4	5.2	3.3	7.2	13.7	1.1	1.0	1.1
	Quiyang	94.07.15 ~96.07.15	-	-	-	167.5	11.0	-	4.9	43.8	3.0	0.5	1.3	13.5	1.7	0.5	0.2
	Taiyuan	94.07.20 ~98.06.10	10.5	57.6	2.2	132.4	11.1	-	6.5	99.4	8.5	7.4	12.2	36.5	2.7	1.3	2.8
	Beijing	95.12.01 ~97.06.04	-	-	-	76.3	21.9	518	6.7	25.0	2.8	1.4	7.0	9.6	0.9	0.5	0.5
	Shanghai	93.06.01 ~99.06.04	16.9	74.7	2.8	28.1	18.2	1049	6.5	33.5	5.6	3.7	4.3	16.8	1.0	0.5	1.8
	Wuhan	94.06.01 ~99.06.03	-	-	-	14.7	9.0	1078	6.5	28.2	6.4	1.9	5.2	11.2	1.0	0.7	0.6
Korea	Daegu	93.08.05 ~99.08.12	14.8	60.9	2.8	14.2	18.7	668	4.9	12.8	2.5	1.1	3.6	2.9	0.3	0.4	0.8
	Daejeon	95.07.30 ~99.06.01	13.1	68.6	2.0	9.1	14.0	1218	4.3	14.9	3.3	3.6	3.7	3.5	0.4	0.4	1.9

The physical properties of the metallic test pieces and marble pieces for exposure test are presented in Table 2. The metallic pieces were prepared with ultrasonically cleaned by acetone and the marble pieces

cleaned by distilled water for a few minutes. After we collected all test pieces from each sampling site, the test pieces were dried in desiccators for 24 hours, and weighed with an accuracy of less than 0.1 mg.

Environmental factors such as temperature, relative humidity (RH) and wind velocity (WV) were collected from the national AWS in each country. Concentrations of SO<sub>2</sub>, NO<sub>2</sub> in the ambient air and the chemical composition of precipitation were also monitored. Long-term (one month) diffusive passive samplers for measuring SO<sub>2</sub> and NO<sub>2</sub> concentrations were used (Warashina, 1997). The bulk sampling of acidic wet deposition was carried out every month, and the rainfall amount at the time of sampling was recorded. The items of wet analysis were pH, electrical conductivity (E.C.), SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>. pH was measured by glass electrode method, E.C. by electric conductivity meter, and anions and cations by ion chromatography.

### 3. RESULTS AND DISCUSSIONS

The annual average environmental factors such as meteorological factors and air pollutants and wet deposition related measurement data are summarized in Table 3. These annual average values were calculated on the basis of the data during seven years from 1993 to 1999, although the averaging periods were different with the sampling sites. The temperature data showed almost similar range around the Northeast Asia, while Daegu, Daejeon and Taiyuan sites showed relatively low values. The RH (relative humidity) was appeared to be low in urban sites such as Tokyo and Osaka in Japan. In addition, RH at Daegu site in Korea was appeared to be a little lower than Daejeon site in Korea.

The WV (wind velocity) was very low (about 1~2 m/s) at the heavy polluted areas such as Chongqing and Taiyuan in China, which was likely to make the air quality of those sites worse. In fact, SO<sub>2</sub> concentration in these China sites were appeared to be very high compared to other sites, and the amounts of SO<sub>4</sub><sup>2-</sup> and Ca<sup>2+</sup> in wet deposition data were also higher in these sites.

The SO<sub>2</sub> concentration with each sampling site could

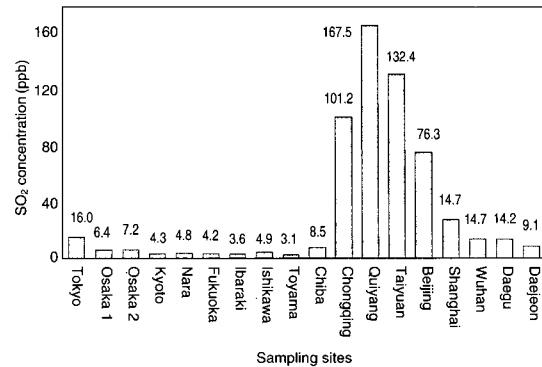


Fig. 2. Comparison of SO<sub>2</sub> concentration with sampling sites.

be compared in Fig. 2 more clearly. The average SO<sub>2</sub> concentration for several years by one-month average was appeared to be 167.5 ppb in Quiyang, 132.4 ppb in Taiyuan, and 101.2 ppb in Chongqing. On the other hand, most of sites in Korea and Japan except Tokyo and Daegu sites showed the lower SO<sub>2</sub> concentration below 10 ppb.

Of two Korean sites, Daegu site showed a little higher SO<sub>2</sub> concentration than Daejeon site. More detail analyses such as monthly variation of SO<sub>2</sub> and NO<sub>2</sub> concentration with the sampling sites could be found in our other paper (Warashina (2001)).

On the other hand, we could see the higher NO<sub>2</sub> concentration at the urban areas in Japan because of its emission characteristics caused to the vehicles (See Table 3). Even though the two Korean sites were also located in suburb areas, the SO<sub>2</sub> and NO<sub>2</sub> concentrations were appeared to be comparatively low because the sampling sites were located at the relatively clean university campus.

One more thing we can say about the chemical composition of wet deposition would be ammonium ion, the concentration of which showed much higher value in Korea and China than Japan, the reason have not yet been clear though.

The corrosion rate of each test pieces was estimated based on the weight loss after exposure to the atmosphere, which was calculated by the following equation.

**Table 4. The average value of annual material corrosion rates in East Asia.**

Sampling site	Period	Corrosion rate (µm/year)										
		Bronze		Ancient copper		Copper		Steel		Marble		
		out	in	out	in	out	in	out	in	out	in	
Japan	Tokyo	93.06.02 ~99.06.01	1.84	0.67	1.45	0.38	1.53	0.47	34.33	18.90	7.14	–
	Osaka 1	93.06.01 ~99.06.01	1.15	0.59	0.96	0.40	0.99	0.42	22.42	15.75	4.20	1.09
	Osaka 2	94.06.01 ~99.06.01	1.31	0.89	1.15	0.68	1.04	0.55	29.12	23.54	–	0.90
	Kyoto	93.06.01 ~99.06.01	0.70	0.23	0.65	0.16	1.31	0.15	24.28	6.39	5.68	0.27
	Nara	93.06.01 ~96.06.01	1.41	0.60	1.11	0.40	1.17	0.40	24.29	11.24	4.66	0.70
	Fukuoka	97.06.01 ~99.06.01	1.17	–	–	–	1.35	0.34	35.51	10.80	6.75	0.66
	Ibaraki	93.06.01 ~99.06.01	1.28	0.25	0.96	0.24	1.04	0.22	25.74	5.85	5.32	0.20
	Ishikawa	93.06.01 ~99.06.01	1.79	0.97	1.67	0.49	1.48	0.59	28.11	14.21	7.94	1.20
	Toyama	97.06.01 ~99.06.01	1.75	–	–	–	1.26	0.99	28.40	24.17	7.15	–
	Chiba	93.06.01 ~99.06.01	2.87	0.61	0.90	0.34	1.70	0.45	42.21	16.21	7.86	–
China	Chongqing	93.06.04 ~99.06.02	5.48	2.84	6.01	2.26	4.55	1.55	143.68	29.79	18.76	3.37
	Quiyang	94.07.15 ~95.06.01	6.17	2.32	7.83	2.01	7.46	1.85	254.60	16.88	–	–
	Taiyuan	95.06.07 ~99.06.10	1.14	0.18	1.35	0.13	1.09	0.22	45.46	5.09	5.21	0.54
	Beijing	93.06.01 ~95.06.01	–	–	0.96	–	0.97	–	24.83	–	–	–
	Shanghai	93.06.01 ~99.06.01	2.07	1.19	2.25	0.77	2.02	0.69	63.60	38.24	9.17	2.87
	Wuhan	95.06.01 ~99.06.01	1.13	0.29	1.02	0.19	1.01	0.32	30.92	10.11	5.33	–
Korea	Daegu	93.08.05 ~96.06.01	1.65	0.64	2.02	0.47	1.75	0.52	49.18	20.79	6.79	–
	Daejeon	95.07.30 ~99.06.01	0.94	0.44	0.92	0.32	1.29	0.72	26.40	8.95	4.72	0.36
	Mean		1.99	0.85	1.95	0.62	1.83	0.62	51.84	16.29	7.11	1.21
	Out/In		2.34		3.15		2.95		3.18		5.88	

\*out: unsheltered exposure, \*\*in: rain-sheltered exposure

$$\text{eroded layer } (\mu\text{m/yr}) = \frac{10 \times \text{Corrosion weight loss (mg)}}{\text{Surface area (cm}^2\text{)} \times \text{specific gravity (g/cm}^3\text{)}}$$

As presented in Table 4, the average corrosion rates of the unsheltered outdoor samples were generally larger than those of rain-sheltered test pieces. The ratio of the corrosion rate of unsheltered test pieces to rain-

sheltered ones was ranging from 2.34 for bronze to 5.88 for marble, which might reflect the effect of wet deposition on material damage.

The corrosion rates in the unsheltered outdoor test pieces were in the order of carbon steel (51.84 µm/year) > marble (7.11 µm/year) > bronze (1.99 µm/year) ≥ ancient copper (1.95 µm/year) > pure copper (1.83 µm/year). In particular, the corrosion rate of steel was

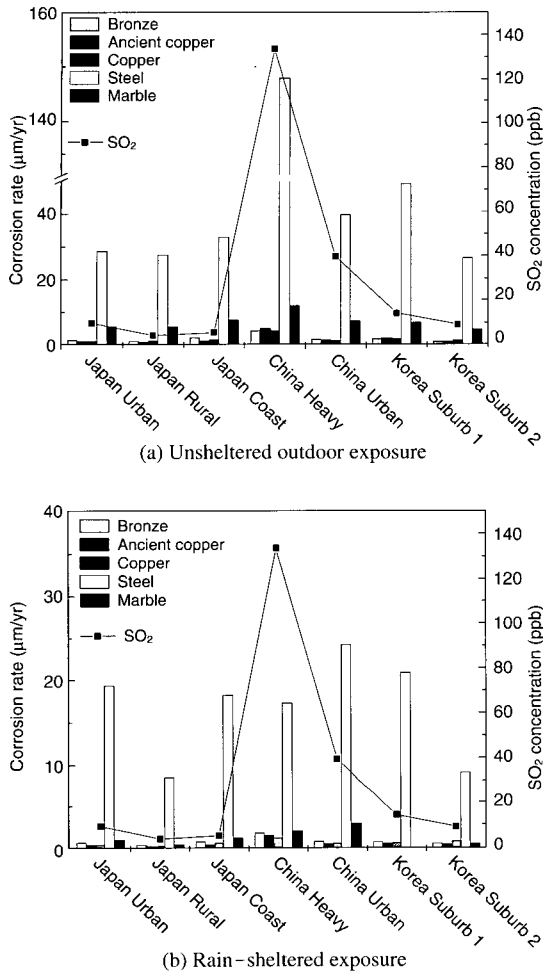


Fig. 3. The corrosion rates of test pieces in unsheltered outdoor (a) and rain-sheltered outdoor exposure (b). The straight line represents the SO<sub>2</sub> concentration.

remarkably larger than other test pieces, which was estimated about twenty to thirty times larger compared to bronze or copper.

Even though it was difficult to tell the difference of corrosion rates between bronze and copper in unsheltered outdoor condition, the corrosion rate of bronze in rain-sheltered indoor condition was appeared to be slightly higher than that of copper. In case of the corrosion rate of marble, the difference of corrosion rate between unsheltered condition and rain-sheltered con-

dition was appeared to be significant. While the corrosion rate of marble in unsheltered condition was 7.11 µm/year, the corrosion rate in rain-sheltered condition was 1.21 µm/year, about six times larger. This result should explain that the corrosion of marble was much more affected by wet deposition.

As for the sampling sites in Fig. 3, the corrosion rates of unsheltered test pieces at the heavily polluted area in China were appeared to be much larger compared to other sites, which might be associated with the high SO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup> concentration. The results of correlation analysis between the corrosion rate and SO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup> concentration will be discussed later.

The corrosion rates at Japan coast sites were comparatively high considering that the levels of SO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup> concentration were low, especially in rain-sheltered condition, which might be attributed to the effect of sea salt. Among three Japan coast sites, comparatively high Cl<sup>-</sup> concentration but low SO<sub>2</sub> concentration was observed at Ishikawa and Toyama site (See Table 3). However, we could see comparatively high concentration not only for Cl<sup>-</sup> but also for SO<sub>2</sub> at Chiba site, which was located near Tokyo. Consequently, the corrosion rate at Chiba site seemed to be higher than Ishikawa and Toyama sites (See Table 4), which might be assumed to indicate the degree of sea-salt effect.

Except these two areas like the heavy polluted sites in China and the seacoast sites in Japan, it seemed to be difficult to discriminate the characteristic difference of corrosion rate with each sampling sites in Japanese and Korean urban and suburb areas. However, it could be said that the corrosion rates at Daegu (Korea suburb 1) site were slightly higher than Daejeon (Korean suburb 2) site.

In order to investigate the characteristics of corrosion rate of test materials with sampling sites, we calculated and summarized the relative corrosion ratio with the sampling sites in Table 5. The figures in Table 5 indicate the comparative corrosion ratio with the sampling sites, which were calculated on the condition that the corrosion rates at Japan rural site was considered as the unit value. In other words, the relative corrosion ratio

**Table 5. The relative corrosion ratio with each sampling site based on the corrosion rate at Japan rural site.**

	Japan ( <sup>out</sup> / <sub>in</sub> <sup>**</sup> )			China ( <sup>out</sup> / <sub>in</sub> <sup>**</sup> )		Korea ( <sup>out</sup> / <sub>in</sub> <sup>**</sup> )	
	Urban	Rural	Coast	Heavy	Urban	Daegu	Daejeon
Bronze	1.25/1.99	1.00/0.00	1.87/2.18	3.73/4.94	1.40/2.06	1.45/1.77	0.83/1.22
Ancient copper	1.31/1.82	1.00/1.00	1.42/1.55	5.59/5.49	1.56/1.79	2.24/1.77	1.02/1.20
Copper	0.98/1.72	1.00/1.00	1.21/2.42	3.59/4.33	1.10/1.81	1.44/1.86	1.06/2.59
Steel	1.04/2.26	1.00/1.00	1.20/2.12	5.39/2.01	1.45/2.82	1.79/2.43	0.96/1.04
Marble	1.01/2.19	1.00/1.00	1.37/2.64	2.14/4.28	1.29/6.31	1.21/—	0.84/0.80
Mean	1.12/2.00	1.00/1.00	1.41/2.18	4.09/4.21	1.36/2.96	1.63/1.96	0.94/1.37

\*out: unsheltered exposure, \*\*in: rain-sheltered exposure

with each sampling site means how many times larger the corrosion rate of each sampling site was compared to that of Japan rural site in which the corrosion rate and air pollutant concentration was found to be generally to be the lowest.

As mentioned earlier, the relative corrosion ratio at the heavy polluted sites in China were appeared to be the largest, 4.09 for unsheltered condition and 4.21 in rain-sheltered condition. This high relative corrosion ratio must be very significant in terms of the effect on cultural properties and of economic loss of material damage. Japan coast site was also showed higher relative corrosion ratio that might be due to the effect of sea-salt.

For China urban site, Japan urban site and Korea suburb site, the relative corrosion ratio in rain-sheltered condition was always higher than that in the unsheltered condition. It could be understood that the corrosion rate in rain-sheltered condition at Japan rural site was showing comparatively lower corrosion rate compared to the corrosion rate in unsheltered condition, which might be due to the very low SO<sub>2</sub> concentration in these areas.

In case of two Korean sites, the relative corrosion ratio at Daegu site was appeared to be apparently higher than Daejeon, which might be associated with the fact that SO<sub>2</sub> concentration at Daegu site was higher than Daejeon. The difference of the corrosion rate between Daegu and Daejeon was similar the difference of SO<sub>2</sub> concentration between these two sites: 14.2 ppb for Daegu, and 9.1 ppb for Daejeon (see Table 3).

The correlation analyses between environmental factors and material corrosion rates were shown in Table 6. In particular, many high correlation coefficients could be found between the chemical species, for example 0.86 between SO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup> concentration, 0.89, 0.94, 0.85 between SO<sub>4</sub><sup>2-</sup> concentration and NH<sub>4</sub><sup>+</sup>, Ca<sup>++</sup> and Mg<sup>++</sup>, respectively. However, the correlation coefficient of relative humidity and NO<sub>2</sub> concentration to other factors was appeared to be low, and rainfall amount showed a slight reverse correlation with some other factors.

On the other hand, we could find comparatively high correlation coefficient between SO<sub>2</sub> or SO<sub>4</sub><sup>2-</sup> concentration and the material corrosion rate in unsheltered exposure condition. The correlation coefficient between SO<sub>2</sub> and unsheltered steel corrosion rate was 0.94, which was the largest correlation coefficient in our corrosion experiment data. The correlation coefficient between SO<sub>4</sub><sup>2-</sup> and unsheltered steel corrosion rate was 0.80.

In general, the correlation coefficient between SO<sub>2</sub> or SO<sub>4</sub><sup>2-</sup> concentration and the corrosion rate of test pieces showed higher value in unsheltered outdoor condition than rain-sheltered condition. In addition, the correlations of material corrosion rate between the test pieces were appeared to be generally high. Consequently, it would be not so hard to conclude that material corrosion was affected by SO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup> concentration.

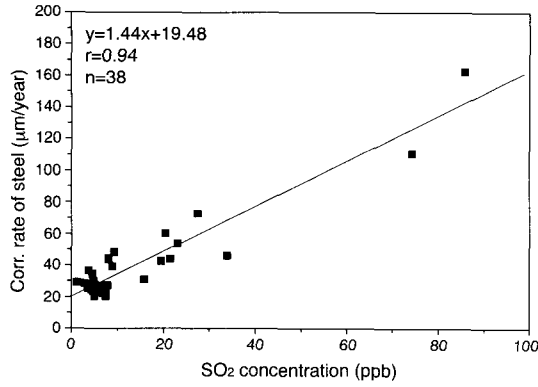
The relationships between SO<sub>2</sub> concentration and the corrosion rates of steel and bronze were shown in

**Table 6. Correlation analysis between environmental factors and material corrosion rates in ambient air.**

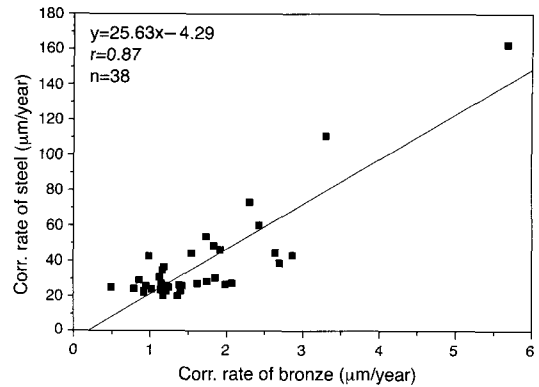
	R.H.	SO <sub>2</sub>	NO <sub>2</sub>	Rainfall	pH	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>	Ca <sup>++</sup>	Mg <sup>++</sup>	K <sup>+</sup>	Na <sup>+</sup>	B-In	A-Out	A-In	C-Out	C-In	S-Out	S-In	M-Out	M-In	
Relative humidity	1.00																						
SO <sub>2</sub>	0.31	1.00																					
NO <sub>2</sub>	-0.62	0.01	1.00																				
Rainfall amount	0.35	-0.28	-0.37	1.00																			
pH	0.28	0.44	-0.08	-0.25	1.00																		
SO <sub>4</sub> <sup>2-</sup>	0.18	0.86	0.00	-0.39	0.59	1.00																	
NO <sub>3</sub> <sup>-</sup>	0.07	0.63	-0.01	-0.46	0.58	0.84	1.00																
Cl <sup>-</sup>	0.13	0.17	-0.31	0.26	0.12	0.30	0.30	1.00															
NH <sub>4</sub> <sup>+</sup>	-0.06	0.69	0.12	-0.50	0.56	0.89	0.90	0.22	1.00														
Ca <sup>++</sup>	0.23	0.75	-0.03	-0.36	0.76	0.94	0.79	0.32	0.79	1.00													
Mg <sup>++</sup>	0.27	0.73	-0.23	-0.18	0.61	0.85	0.72	0.59	0.68	0.87	1.00												
K <sup>+</sup>	0.27	0.72	-0.22	-0.36	0.63	0.85	0.78	0.39	0.80	0.79	0.82	1.00											
Na <sup>+</sup>	0.13	-0.05	-0.32	0.40	-0.09	0.02	0.04	0.92	-0.06	0.05	0.38	0.13	1.00										
Bronze-Out*	0.11	0.73	0.12	-0.01	0.48	0.55	0.49	0.35	0.43	0.52	0.51	0.56	0.21	1.00									
Bronze-In**	-0.44	0.16	0.29	0.33	-0.10	0.16	0.00	0.34	0.16	0.11	0.15	-0.10	0.39	0.42	1.00								
Ancient Copper-Out	-0.38	0.46	-0.08	-0.01	0.18	0.26	0.31	0.10	0.22	0.20	0.20	0.29	0.14	0.59	0.31	1.00							
Ancient Copper-In	-0.38	0.26	0.45	0.03	-0.02	0.27	0.13	0.16	0.35	0.19	0.11	-0.13	0.18	0.22	0.82	0.18	1.00						
Copper-Out	0.31	0.87	-0.02	-0.04	0.53	0.72	0.62	0.25	0.57	0.66	0.56	0.70	0.06	0.88	0.25	0.78	0.02	1.00					
Copper-In	0.06	0.46	-0.02	0.23	0.11	0.50	0.45	0.34	0.47	0.41	0.45	0.34	0.31	0.47	0.83	0.50	0.85	0.51	1.00				
Steel-Out	0.30	0.94	0.02	-0.14	0.60	0.80	0.66	0.20	0.64	0.74	0.60	0.76	-0.06	0.87	0.18	0.70	0.13	0.95	0.44	1.00			
Steel-In	0.05	0.46	0.29	0.02	0.49	0.64	0.47	0.32	0.53	0.68	0.57	0.34	0.27	0.58	0.62	0.45	0.61	0.46	0.51	0.59	1.00		
Marble-Out	0.45	0.88	-0.14	0.03	0.35	0.64	0.26	0.19	0.36	0.60	0.63	0.44	0.18	0.55	0.53	0.43	0.41	0.59	0.23	0.56	0.55	1.00	
Marble-In	-0.34	0.34	0.46	0.00	0.06	0.34	0.23	0.22	0.31	0.29	0.32	0.26	0.17	0.35	0.64	0.30	0.53	0.19	0.28	0.26	0.47	0.22	1.00

\*out: unsheltered exposure, \*\* in: sheltered exposure

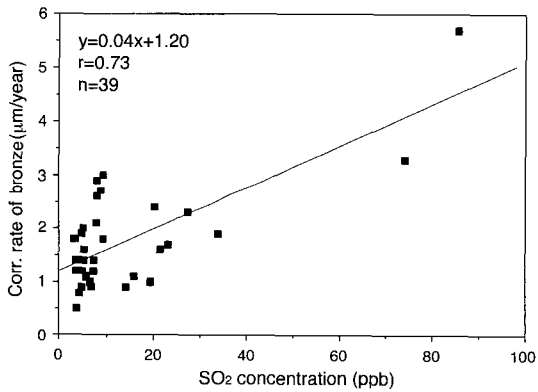




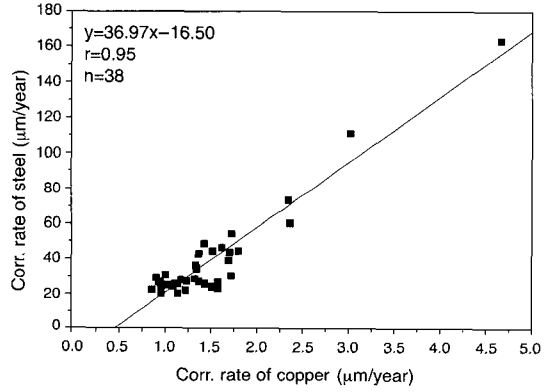
(a) Between SO<sub>2</sub> concentration and steel



(a) Between steel and bronze



(b) Between SO<sub>2</sub> concentration and bronze



(b) Between steel and copper

**Fig. 4. The regression analysis between SO<sub>2</sub> concentration and the corrosion rates of (a) steel and (b) bronze.**

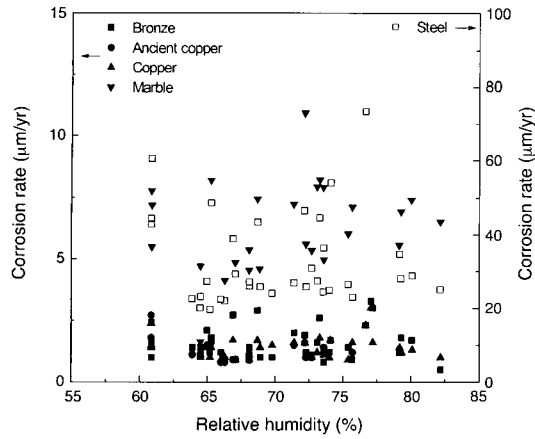
**Fig. 5. The correlation of the corrosion rates between each test piece.**

Fig. 4. With the regression equations in Fig. 4, the yearly material corrosion rates affected by SO<sub>2</sub> concentration were estimated as 1.44 µm/year/SO<sub>2</sub> (ppb) for steel, and 0.04 µm/year/SO<sub>2</sub> (ppb) for bronze.

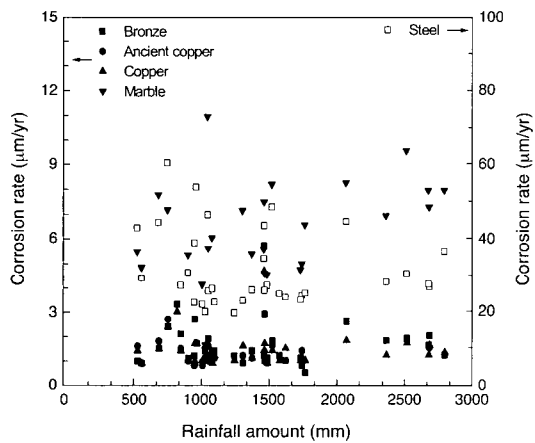
The relationship between the corrosion rates of steel and other test pieces was presented in Fig. 5. As the results, the correlation coefficient between steel and bronze, and between steel and copper was appeared to be 0.87 and 0.94, respectively. In conclusion, the corrosion rate between each test piece has a deep relevance to SO<sub>2</sub> concentration. With these results that steel has a very large corrosion rate and has a high correlation

with other materials in this study, it might be possible to conclude that steel would be a very good indicator for the evaluation of material damages by air pollution.

The material corrosion is also caused to not only air pollution but also the meteorological factors (Kirkitsos and Sikiotis, 1995). In this paper, we confined our investigation to the relationships between the corrosion rate and relative humidity or rainfall, which was shown in Fig. 6. In general, it was difficult to find the typical relationship between these factors, the correlation coefficient of which was also low shown in Table 6. However, we could see a little correlation between material damage and relative humidity and rainfall amount for



(a) Between the corrosion rate and relative humidity



(b) Between the corrosion rate and rainfall amount

**Fig. 6** The relationship between the corrosion rate of the unsheltered test pieces and relative humidity and rainfall amount.

the steel and marble. From now on, these relationships should be studied with more accurate experiment data by chamber or field experiment.

#### 4. CONCLUSIONS

The material exposure experiments have been carried out to evaluate the relationship between air pollution and material corrosion rate with the cooperation of

the researchers in Japan, China, and Korea since 1993.

As the results, it was found that the corrosion rates of test pieces in the ambient air were appeared to be in the order of carbon steel (51.84  $\mu\text{m}/\text{year}$ ) > marble (7.11  $\mu\text{m}/\text{year}$ ) > bronze (1.99  $\mu\text{m}/\text{year}$ )  $\geq$  ancient (1.95  $\mu\text{m}/\text{year}$ ) > pure copper (1.83  $\mu\text{m}/\text{year}$ ). In addition, the corrosion rates of unsheltered test pieces were ranging from 2.34 times for bronze to 5.88 times for marble than to rain-sheltered ones. It could be said that steel was a very good indicator for the evaluation of material damages by air pollution considering that steel was very sensitive to air pollution and had a good correlation with other test pieces.

It was also found that the corrosion rate in the heavy polluted area in China was the highest, and the corrosion rates of the metal pieces were generally proportional to  $\text{SO}_2$  concentration. Between two sites in Korea, the test pieces at Daegu site were likely to be more affected by  $\text{SO}_2$  concentration.

With the regression analysis, the yearly material corrosion rates affected by  $\text{SO}_2$  concentration were estimated as 1.44  $\mu\text{m}/\text{year}/\text{SO}_2$  (ppb) for steel, and 0.04  $\mu\text{m}/\text{year}/\text{SO}_2$  (ppb) for bronze.

The damage on the cultural properties will be very important economically and culturally. At last, it must be necessary to enlarge the cooperation for the air pollution related study and counteract measures among the East Asian countries.

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