

C-4.2 Studies on effects of acid depositions to cultural assets and industrial materials in China, Hong Kong, Korea and Japan

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Abstract

The impact of wet and dry deposition of acid components to cultural assets, building and industrial materials was investigated on several materials: bronze, copper, carbon steel, marble etc., by exposing under indoor and outdoor conditions at regional levels in China, Hong Kong, Korea and Japan. Different corrosion products were formed, depending on the regional pollution and climate. The concentrations of SO<sub>2</sub> and NO<sub>2</sub> were the most effective factor for the formation of copper corrosions. The corrosion rates have been evaluated. Significant corrosions were found in the sites in China. Thermo-humidistatic chamber experiments have been carried out for quantitative analysis of deteriorations of materials by meteorological elements and air pollutions. Damages of cultural assets were investigated in China and Japan.

Key Words Cultural Asset, Acid Deposition, Exposure Experiment, Materials, Thermo and Humidistatic Chamber

1. Introduction

The industrial activities of man have given a new dimension to environmental science. Until about 1960 the only effects causing strong concern occurred within a few kilometers of the sources of emission. Recently, many pollutants exhausted are being transported and transformed over large distance and are affecting ecosystems in many countries(ref.1-3), for example in acid rain. Today, therefore, everyone seems to be concerned about global hazards due to acid rain damages to forests, death of fish in lakes and ponds, and damage to buildings, and damage to cultural properties.

An International Cooperative Programme (ICP) was started to evaluate the effect of airborne acidifying pollutants on corrosion of materials in September 1987 and involved exposure tests at 39 test sites in 12 European countries, the United States and Canada (ref.1). Since June 1993, materials of cultural properties were exposed to acid deposition in eastern Asia by Cultural Properties and Materials Damage by Air

Pollution Committee (Subcommittee of Japan Society for Atmospheric Environmental (JSAE)).

## 2. Research Objective

The quantitative damage of cultural assets, building and industrial materials, caused by acidic air pollutants in eastern Asia, has been measured during the exposure to wet and dry acidic deposition and relation between the rate of damage of materials and the concentration of pollutants and climates are discussed.

## 3. Chamber Experiments

The objective of this study is to determine quantitatively the effects of atmospheric acidic deposition (i.e., acidic-precipitation and acidic gases) on the materials used for cultural artifacts, through exposure experiments conducted in a specially designed.

### 3.1 Experimental method

#### 3.1.1 Preparation of test pieces

The materials, sizes and surfaces for test pieces are shown in Table 1. The metallic test pieces were ultrasonically cleaned with acetone for a few minutes. The marble pieces were ultrasonically cleaned with distilled water for a few minutes and dried in a desiccator for 24 hours. The test pieces were accurately weighed (less than 0.1 mg) and stored in a desiccator.

Table 1. Test pieces.

materials	exposure	size	Ingredients	surface	experlaental sites
bronze	unsheltered rain-sheltered leaching	2.0×30×40 mm	JIS-H-5111 BC6 Cu85%, Sn5%, Pb5%, Zn5%	#400 treatment	21 sites in Japan, Korea . China and Hong Kong
old type copper	unsheltered rain-sheltered	0.8×30×40 mm	reproductions of Budder hole's roof in Todaiji Cu99.258%, Pb0.58%, As0.02%, Zn0.002%, Fe0.001%	#400 treatment	21 sites in Japan, Korea . China and Hong Kong
pure copper	unsheltered rain-sheltered	0.4×30×40 mm	JIS-H-3100 C1201P Cu>99.9%	#400 treatment	21 sites in Japan, Korea . China and Hong Kong
steel	unsheltered rain-sheltered	1.2×30×40 mm	JIS-G-3141 SPPC	#400 treatment	21 sites in Japan, Korea . China and Hong Kong
marble	unsheltered rain-sheltered	5.0×20×20 mm	Italian white marble		21 sites in Japan, Korea . China and Hong Kong
cedar	unsheltered	10×70×70 mm	from Yoshino		9 sites in Beijing, Chong qing, Shanghai, Taejon, Tok yo, Osaka(3), Nara, Kyoto
cypress	unsheltered	10×70×70 mm	from Iiso		9 sites in Beijing, Chong qing, Shanghai, Taejon, Tok yo, Osaka(3), Nara, Kyoto
urushi Japanese lacquer	rain-sheltered	7.0×50×50 mm	foundation material: hiba(cypress) foundation layer: coated with urushi with clay and iron powder. surface layer: coated with urushi with charcoal powder two times.		9 sites in Beijing, Chong qing, Shanghai, Taejon, Tok yo, Osaka(3), Nara, Kyoto

### 3.1.2 Exposure experiments

As shown in Fig. 1, all exposure were performed by placing two little chambers inside of the constant-temperature both, standard gases used for the experiments were purified air, O<sub>3</sub>, SO<sub>2</sub> and NO<sub>2</sub>.

Each gas flow rate was controlled by a mass flow controller so as to make a pre-determined concentration of each gas and mixture of gases by mixing it or there with purified air.

By a sampling part as well as temperature or humidity sensors outside of the chamber, the gas concentrating, temperature and relative humidity data were taken and stored in a data-translation PC.

### 3.1.3 Experimental condition

All exposure experiments were performed in the following steps; first, placing the 5 kinds of the materials inside the chamber; second, controlling the temperature and humidity at a level; and third, introducing a single gas or a mixture of gases with fixed concentrations into the chamber.

#### (1) Exposure experiment with single gases.

Standard gases: purified air, O<sub>3</sub>(1ppm), O<sub>3</sub>(1ppm),  
SO<sub>2</sub>(1ppm), NO<sub>2</sub>(10ppm)

Temperature 20°C, relative humidity 60, 70, 80%

Method of exposure: Take out the materials after placing them in the chamber for a week; measure the weight of the materials, performed the ion analysis. Repeat this process for 3 weeks. The materials were also placed for 2 and 3 weeks continuously in the same way as in the case of a week exposure.

#### (2) Exposure experiment with a mixture of gases.

Standard gases: SO<sub>2</sub>(1ppm)+NO<sub>2</sub>(10ppm),  
O<sub>3</sub>(1ppm)+SO<sub>2</sub>(1ppm)+NO<sub>2</sub>(10ppm)

Temperature 20°C, relative humidity 60, 70, 80%

Method of exposure: Performed in the same manner as in the case of single gas exposure.

## 3.2 Results of exposure experiments

Table 2 summarizes the results of the exposure experiments performed on the five types of materials commonly found in cultural artifacts. The order of the weight gain due to the corrosion effects of standard gases were O<sub>3</sub>+SO<sub>2</sub>+NO<sub>2</sub> > SO<sub>2</sub>+NO<sub>2</sub> > NO<sub>2</sub> > O<sub>3</sub> > SO<sub>2</sub> > Air under all the conditions of the experiment, while those of the thickness loss were O<sub>3</sub>+SO<sub>2</sub>+NO<sub>2</sub> > SO<sub>2</sub>+NO<sub>2</sub> > NO<sub>2</sub> > O<sub>3</sub> > Air > SO<sub>2</sub>.

The Weight gain were in the order of steel > marble > bronze = old type copper > pure copper under every experimental condition. The similar trends were observed in the thickness loss as well.

In one-week exposure experiments with standard gases, the weight gain occurred in every types of the materials, while the thickness loss did not occur with SO<sub>2</sub> and NO<sub>2</sub> gases.

All materials were subjected to Ultra-sonic extraction in order to perform ion analysis on them after each consecutive or continuous exposure has been completed.

In this extraction process, the marble samples of consecutive

exposures experienced cracks on them and their measured weights in the 2nd-week and 3rd-week exposures indicated a negative weight gain. Therefore, results of the continuous exposures alone were tabulated below.

The results indicated that the weight gain due to corrosion increase as the exposure duration increased in the order of  $\text{NO}_2 > \text{O}_3 > \text{SO}_2$ . For air, the reverse was true.

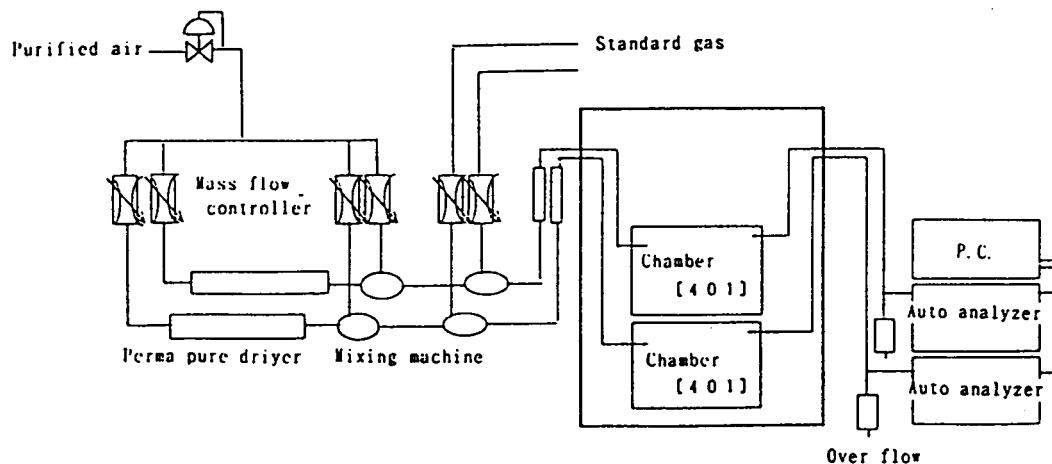


Fig. 1. Schematic diagram of experimental apparatus.

Table 2. Exposure experiment by standard gases.

condition	expo. gas	puri. air		O <sub>3</sub>		SO <sub>2</sub>		NO <sub>2</sub>		SO <sub>2</sub> +NO <sub>2</sub> +O <sub>3</sub>		SO <sub>2</sub> +NO <sub>2</sub>					
		gain mg/dm <sup>2</sup>	loss μm	gain mg/dm <sup>2</sup>	loss μm	gain mg/dm <sup>2</sup>	loss μm	gain mg/dm <sup>2</sup>	loss μm	gain mg/dm <sup>2</sup>	loss μm	gain mg/dm <sup>2</sup>	loss μm				
1 week 20°C 60%	bronze		0.05		1.0		0.12				2.9		12	0.23	2	0.07	
	old copper		0.03		0.8		0.05				1.7		8	0.18	2	0.07	
	pure copper		0.04		1.2		0.05				1.7		10	0.21	2	0.06	
	steel	0.1	0.17	5.7	0.45					15.0		120	2.30	77	1.70		
	marble	0.5		1.1		0.7				2.9		8	0.64	2			
	3 times	bronze	0.3	0.11	1.6	0.17		0.05		4.8	0.17	17	0.31	5	0.07		
		old copper	0.4	0.06	1.1	0.09	0.4	0.04		3.5	0.15	19	0.39	5	0.09		
		pure copper	1.3	0.06	1.6	0.09	0.7	0.04		3.7	0.13			4	0.09		
		steel	0.3	0.24	8.7	0.53	1.5	0.27		22.0	1.40	220	5.10	150	3.10		
		marble								3.6		15					
	3 week 20°C 80%	bronze		0.15	1.9	0.21	0.6	0.08		8.3	0.30	35	0.39	39	0.35		
		old copper	0.2	0.09	1.5	0.12	0.9	0.07		6.4	0.24	23	0.56	43	0.68		
pure copper		0.4	0.09	2.0	0.11	1.3	0.07		5.6		0		40	0.66			
steel		2.6	0.32			3.3	0.48		34.0	2.00	280	5.60	260	5.80			
marble											33		18				
2 weeks continuous	bronze		0.04	1.3	0.09		0.02		4.4	0.22	28	0.52	6	0.13			
1 week 20°C, 60%	old copper		0.03	1.2	0.05	0.3	0.02		3.7	0.12	22	0.46	6	0.12			
1 week 20°C, 60%	pure copper		0.03	1.2	0.05	0.3	0.03		3.8	0.10	23	0.48	5	0.10			
2 week 20°C, 70%	steel			7.6	0.49	1.4	0.09		34.0	1.90	440	11.00	240	4.60			
2 week 20°C, 70%	marble	0.3		1.9		0.8			5.3		22		8				
3 weeks continuous	bronze		0.04	1.2	0.09	0.9	0.02		6.0	0.21	49	0.68	36	0.46			
1 week 20°C, 60%	old copper		0.03	1.7	0.06	1.0	0.03		6.9	0.17	49	0.81	29	0.54			
1 week 20°C, 70%	pure copper		0.03	1.5	0.06	0.6	0.01		4.9	0.13	41	0.73	28	0.55			
2 week 20°C, 70%	steel			9.9	0.37				42.0	1.80	680	14.00	313.00				
3 week 20°C, 80%	marble	0.2		2.8		1.2			5.6		69		35				

#### 4. Field Exposure Test

The impact of wet and dry deposition of acid components to cultural assets, building and industrial materials was investigated on several materials: bronze, copper, carbon steel, marble etc., by exposing under indoor and outdoor conditions at regional levels in China, Hong Kong, Korea and Japan.

##### 4.1 Experimental method

###### 4.1.1 Experimental sites

The locations of the 22 sampling sites are shown in Fig. 2. The sites are located in heavily polluted areas in China in Guiyang and Chongqing; urban areas in China in Shanghai, Wuhan, Beijing, Taiyuan and Shenyang; Hong Kong; South Korea in Taejon and Taegu; the Japan Sea coast area in Fukuoka, Ishikawa and Toyama; urban areas in Japan in Tokyo, Chiba and Osaka (3 sites); rural areas in Japan in Nara, Kyoto and Ibaragi; and background in Ichinose.

###### 4.1.2 Preparation of test pieces

The test pieces were same to ones used in chamber experiments.

###### 4.1.3 Exposure method and period

The test pieces were exposed to dry and wet depositions under unsheltered conditions (outdoor), and exposed to dry deposition under rain-sheltered conditions (indoor). Exposed periods were 3-4 months (short exposure) for checking the direct impact of acid pollutants, and 1, 2 and 4 years (long exposure) for checking the characteristic impact of the individual sites (from June 1993 through February 1997).

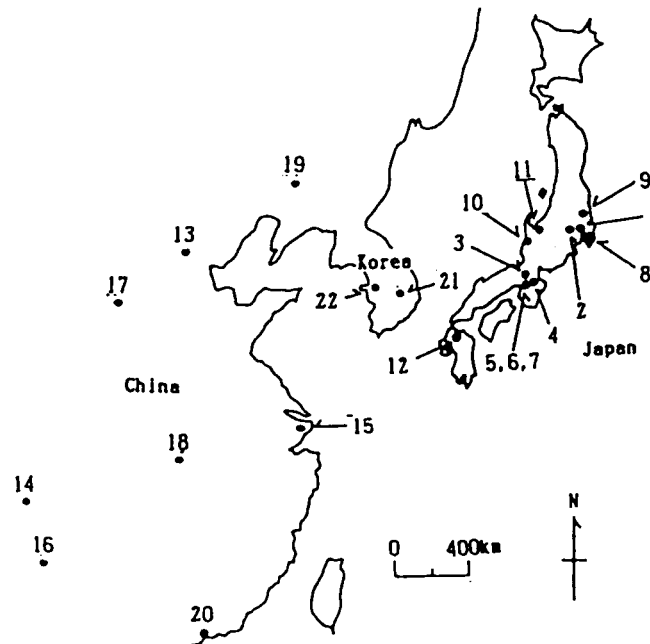


Fig. 2. The location of the 22 sampling sites.

1:Tokyo, 2:Ichinose, 3:Kyoto, 4:Nara, 5:Osaka Sakai, 6:Osaka Konohana, 7:Osaka Higashinari, 8:Chiba, 9:Ibaragi, 10:Ishikawa, 11:Toyama, 12:Fukuoka, 13:Beijing, 14:Chongqing, 15:Shanghai, 16:Guiyang, 17:Taiyuan, 18:Wuhan, 19:Shenyang, 20:Hong Kong, 21:Taegu, 22:Taejon

#### 4.1.4 Analytical procedure

The exposed test pieces were collected after every 3-4 months and optically examined by using a Keyence (Osaka, Japan) VH-6200 digital microscope. The corrosion products on the pieces were identified by using a Rigaku (Tokyo, Japan) RINT 1500 X-ray diffractometer (Target: Cu, X-ray power: 40 KV x 150 mA). The pieces of bronze and coppers were immersed in a 10% ammonium-thioglycolic-acid solution at 80 °C for about 10 minutes. The carbon steel pieces were immersed in a boiling 10% di-ammonium-hydrogen-citrate solution repeatedly. The marble pieces were dried in a desiccator for 24 hours. Weight were measured with an accuracy of less than 0.1 mg.

#### 4.1.5 Environmental factors

Temperature, relative humidity (RH), the time of wetness (TOW) and wind velocity (WV) were recorded. The TOW is defined as the time with RH > 80 % and Temp > 0 °C. Concentrations of SO<sub>2</sub>, NO<sub>2</sub>, O<sub>x</sub> and SPM in ambient air and the chemical composition of precipitation were monitored. Long-term (one month) diffusion samplers for determining SO<sub>2</sub> and NO<sub>2</sub> were used in China and Korea from June 1994, because of difficulty in sampling. Sea-salt was collected by using a cotton gauze collector.

### 4.2 Results and Discussions

#### 4.2.1 Environmental factors

All sites were situated in the temperate climatic zone. The RH was low in South Korea and urban sites in Japan. The WV was about 1 m/sec in winter in heavy polluted sites in China. The concentrations of SO<sub>2</sub> were very high (about 140 ppb) in heavily polluted areas in China, while NO<sub>2</sub> was high in urban areas in Japan (Fig.3). O<sub>x</sub> concentrations were high in spring in the Japan Sea coast area and in rural areas in Japan. TSP was very high in spring in China. Sea-salt and rainfall were very heavy in winter in the Japan Sea coast area. Amounts of SO<sub>4</sub><sup>2-</sup> and Ca<sup>2+</sup> in wet deposition were very high in China (Fig.4).

#### 4.2.2 Corrosion products

The results of X-ray diffraction have shown that CuSO<sub>4</sub>·3Cu(OH)<sub>2</sub> (brochantite) was formed on the copper pieces only after 4 months of outdoor and indoor exposure in China (Fig.5). CuNO<sub>3</sub>·3Cu(OH)<sub>2</sub> (gerhardtite) was formed only on the pieces exposed indoors in urban areas in Japan (Fig.6). Both products were identified in South Korea, but could not be detected in rural area in Japan. PbCO<sub>3</sub>·Pb(OH)<sub>2</sub> (basic lead carbonate) was detected on the bronze pieces exposed outdoors in rural areas. Regarding on the carbon steel pieces, alpha type FeOOH (goethite), gamma type FeOOH (lepidocrocite) and alpha type Fe<sub>2</sub>O<sub>3</sub> (hematite) were formed in Japan. Furthermore Fe<sub>3</sub>O<sub>4</sub> (magnetite) was identified in China only after 4 month's exposure. CaSO<sub>4</sub>·2H<sub>2</sub>O (gypsum) was formed on the surface of the marbles exposed indoors in all sites, but no gypsum could be detected on the specimens exposed outdoor because gypsum was more soluble than CaCO<sub>3</sub> (calcite).

### 4.2.3 Corrosion rates

The corrosion rates in 1 year's exposure are shown in Table 3. The rates were estimated on the basis of thickness losses. The corrosion rate order (outdoor) was carbon steel > marble > old type copper = bronze > pure copper (Fig.7). The rates in outdoor tests were 2-3 times larger than those in indoor ones. Impure copper such as old type copper and bronze is more sensitive to acid deposition than pure copper. Regarding the sites, the order of the corrosion degree (outdoor) were heavily polluted areas in China > urban areas in China > South Korea > the Japan Sea coast area > urban areas in Japan > rural areas in Japan (Fig.7). The corrosion rates were large in summer in Japan, while in winter in China (Fig.8).

### 4.3 Conclusions

The analysis of the atmospheric corrosion tests resulted in the following concepts. Brochantite could be formed on copper at elevated  $\text{SO}_2$  concentrations, and gerhardtite if  $\text{NO}_2$  is present. Carbonates would be formed on bronze in rural atmospheres.  $\text{SO}_2$  contributes significantly to the degradation of marble exposed indoor. It has also been shown that wet deposition and natural dissolution by rain give significant effects on the corrosion. The corrosion rates of carbon steel and marble were much larger (outdoor). Impure copper is more sensitive to acid deposition than pure copper. The material damage was more serious in China than in other countries.

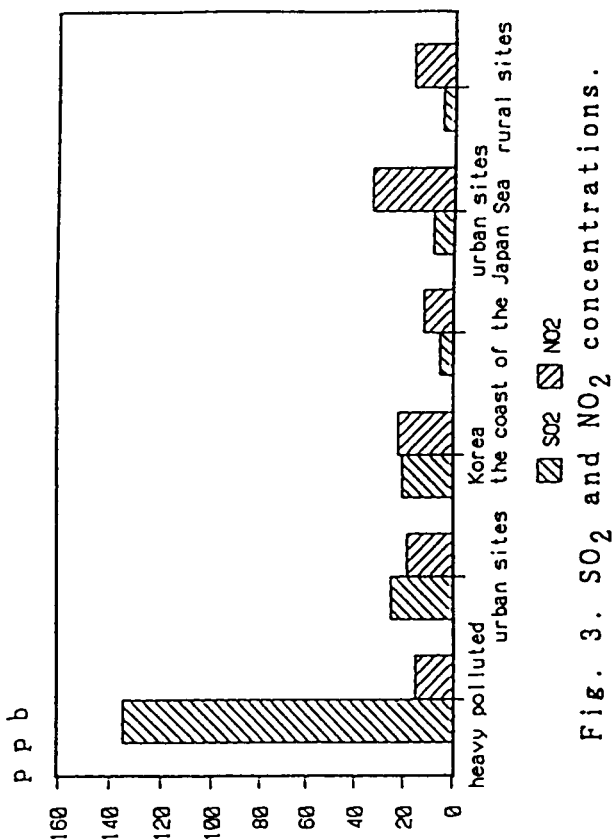


Fig. 3.  $\text{SO}_2$  and  $\text{NO}_2$  concentrations.

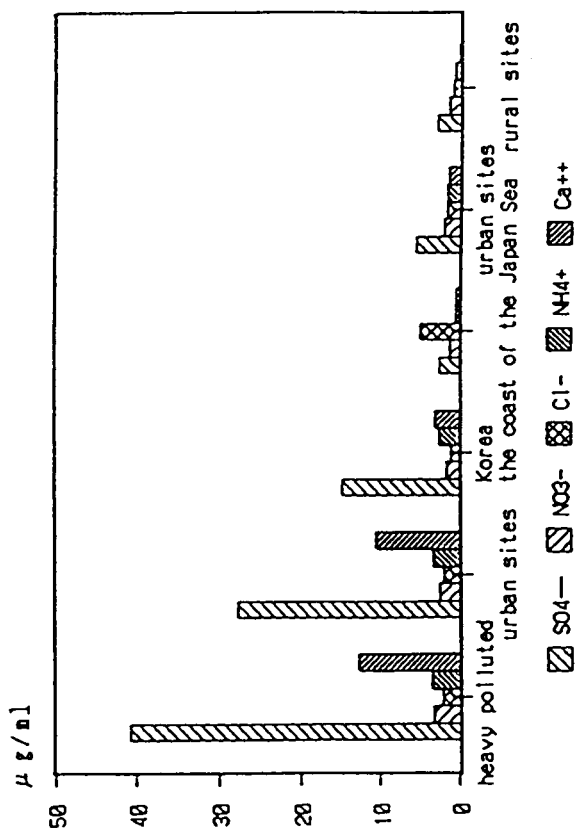


Fig. 4. Wet depositions.

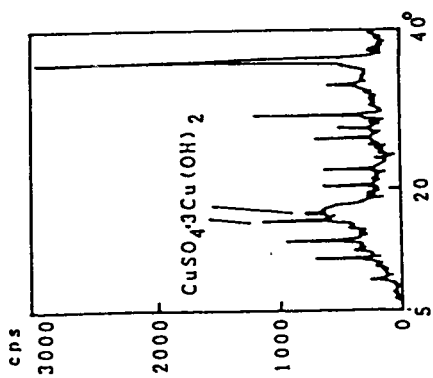


Fig. 5.  $\text{CuSO}_4 \cdot 3\text{Cu}(\text{OH})_2$  (brochantite) on copper outdoors in Chongqing.

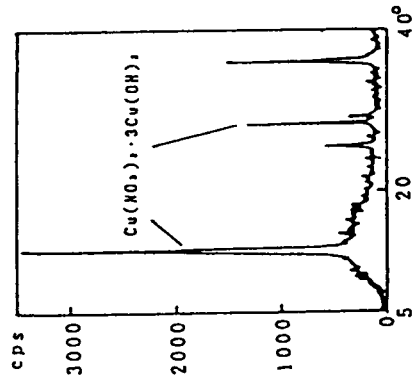


Fig. 6.  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{Cu}(\text{OH})_2$  (gerhardtite) on copper indoors in Osaka.

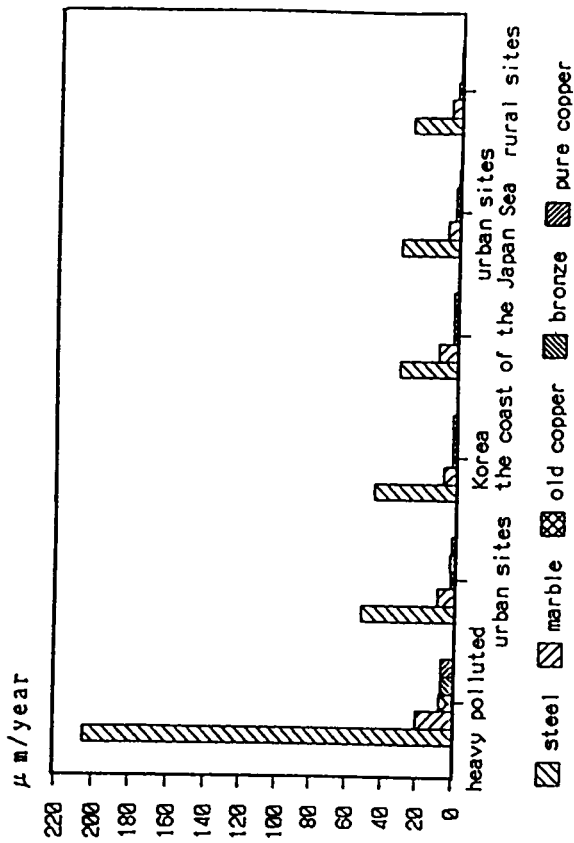


Fig. 7. Corrosion rates (outdoor).

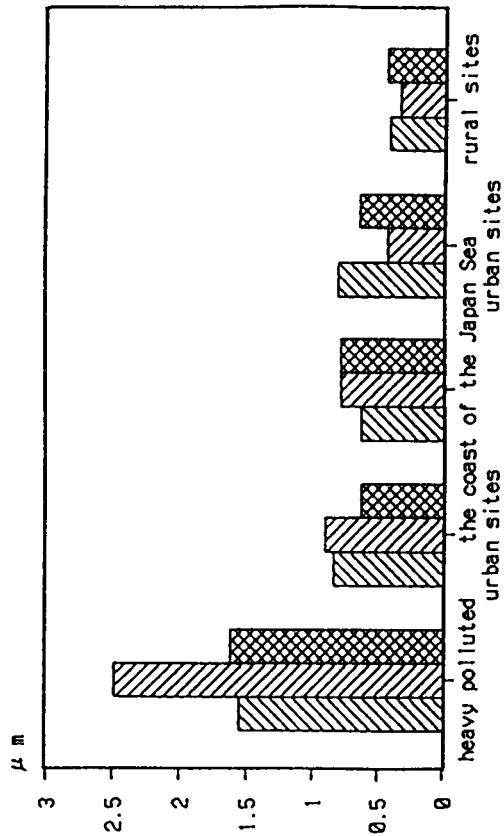


Fig. 8. Seasonal corrosion rates of bronze (outdoor).



Table 3. Corrosion rates.

area	cites	peiod	bronze		old type copper		pure copper		steel		marble								
			out	in	out	in	out	in	out	in	out	in							
			gain	loss	gain	loss	gain	loss	gain	loss	gain	loss							
			μg/dm <sup>2</sup>	μg/dm <sup>2</sup>	μg/dm <sup>2</sup>	μg/dm <sup>2</sup>	μg/dm <sup>2</sup>	μg/dm <sup>2</sup>	μg/dm <sup>2</sup>	μg/dm <sup>2</sup>	μg/dm <sup>2</sup>	μg/dm <sup>2</sup>							
China	heavily polluted	Guiyan	171	0.3	155	2.7	52	8.0	108	2.2	19	7.6	95	2.0	6290	263	-806	22	
		Chongqing	377	6.8	179	3.0	225	6.8	129	2.5	120	5.3	127	2.4	-1180	147	-1360	38	
			281	6.5	194	3.0	157	5.5	133	2.5	120	5.0	128	2.4	-396	107	-1200	30	
		urban	Shanghai	121	2.2	118	1.5	120	2.8	79	1.0	104	2.2	59	0.8	-892	79	-717	53
			Wuhan	52	2.0	60	0.8	50	1.6	61	0.6	47	1.6	50	0.7	-115	48	-947	27
South Korea		Beijing	10	1.3	16	0.3	15	1.2	12	0.3	20	1.2	14	0.4	810	32	-100	10	
							12	0.9											
							22	0.9											
							40												
							23												
Japan	long Kong	Taiyuan	73	1.6	18	0.2	65	1.5	13	0.2	66	1.5	14	0.4	534	46	18	6	
		Shenyang	2		28		18		24		19		23		-172		-22		
			9	2.3	106	2.7	15	1.7	55	1.5	15	1.6	79	2.8	-296	46	1230	44	
			-1	1.0	18	0.4	6	1.1	18	0.4	8	1.1	20	0.4	607	31	-10	9	
			-1	1.7			7	1.9			7	1.6			230	46			
Japan	Sea coast	Taegu	6	1.1			12	1.7			12	1.5			1420	44			
			49		32		59		25		56		26		629		-259		
			2	1.7	32	1.1	19	1.9	32	0.8	21	1.6	36	1.3	1310	46	750	21	
			-2	2.0	37	1.2	3	1.8	18	0.5	0	1.7	20	0.6	720	32	509	13	
			-4	2.1	28	0.8	-5	1.7	22	0.6	-1	1.7	21	0.6	704	28	504	12	
Japan	urban	Toyama	0	2.2	140	1.6	-4	1.5	36	1.5	-3	1.1	40	1.4	845		1030	33	
		Tokyo	3	2.0	32	0.7	3	1.8	23	0.5	11	1.5	25	0.5	245	51	627	19	
			3	1.8	34	0.8	9	1.5	20	0.4	13	1.4	25	0.5	330	39	559	21	
			3	0															
			27	2.8	23	0.6	13		11	0.4	11	3.5	10	0.5	-155	46	458	18	
Osaka		Chiiba	38	3.0	21	0.8	22	1.0	9	0.4	19	3.5	11	0.5	356	45	479	15	
			33	2.7	8	0.6	1	1.1	10	0.4	22	1.9	2		-100	40	346	16	
			-6	1.4	28	0.6	6	1.3	23	0.8	5	1.1	22	0.6	767	27	468	23	
			5	1.3	32	0.9	6	0.9	23	0.9	-28	0.9	22	0.7	511	23	438	25	
			13	2.3	33	0.9	14	1.7	20	0.7	13	1.0	31	0.7	369	30	185	17	
Osaka		Osaka(3)	-14	1.3	32	0.7	-4	1.1	20	0.5	-2	0.9	18	0.3	803	27	415	18	
			-5	1.1	34	0.7	1	1.0	19	0.4	5	1.0	13	0.4	661	23	443	18	
			1	1.4	24	0.5	5	1.1	17	0.4	6	1.1	18	0.5	563	20	424	13	
			-5	1.5	22	0.6	-1	1.2	23	0.5	2	1.1	21	0.5	603	26	448	12	
			6	1.5	24	0.6	7	1.2	21	0.4	10	1.3	20	0.5	583	23	430	11	
Osaka		Kyoto	-13	0.8	10	0.3	-7	1.4	6	0.2	-2	1.1	5	0.2	751	25	285	9	
			16	1.0	8	0.2	6	1.3	7	0.1	11	1.7	6	0.3	720	23	251	6	
							5	1.1			2	1.1	10	0.2	675	27	304	7	
			-1	1.3	8	0.2	7	1.1	8	0.3	8		8	0.4	650	26	278	7	
			4	0.1					0	0.2			3	0.2			44	1	
background	chinese	Osaka(1): Sakai, Osaka(2): Osaka(3): Environmental Pollution Control Center, Osaka Prefecture																	