

C-3.2.3 Studies on the Impacts of Controlling Techniques for the Emission of Acid-Precursors Evaluated in Terms of Material Erosion

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Abstract Atmospheric and experimental corrosion tests were carried out to estimate the levels of complicated air pollution in East Asia. Qualitative and quantitative atmospheric corrosion has been monitored on bronze, copper, steel, marble, cedar, cypress and urushi (Japanese lacquer) plates, exposed to outdoor and indoor airs in cities located in East Asia. Brochantite and cuprite were formed on the copper at the places where the sulfur dioxide concentration was high, and basic cupric nitrate and cuprite were formed at the places where the nitrogen dioxide concentration was high. Gypsum was observed on the pieces exposed to the indoor air at all the sites. No gypsum was found on the pieces exposed to the outdoor air. Numerous fine spots (0.2-0.3 mm in diameter) were observed on the surfaces of the urushi plates exposed at Chongqing, China and Taejon, Korea, where were foggy cities. The effects of atmospheric and meteorological factors on copper and marble plates were estimated by using regression analysis in several cities in East Asia. Of the atmospheric factors, sulfur dioxide is mostly destructive to the materials especially in China and South Korea. The copper plates may be corroded under the natural conditions such as meteorological factors and sea salt in Japan. The copper may be increasingly damaged with the deposition flux of sulfur and chlorine. The marble may be significantly degraded by gaseous sulfur dioxide, but receive no effects of sulfate ion in the rain. The copper plates were tested artificially by (1) immersing them in nitric acid, hydrochloric acid and sulfuric acid solutions, (2) exposing to air including sulfur dioxide, nitrogen dioxide and ozone, and (3) exposing to artificial acid rain under a programmed cyclic condition. Cuprite and/or tenorite were formed on the plates in the immersion test and the artificial acid rain test. Basic cupric nitrate and cuprite were observed in the gas exposure test of sulfur dioxide, nitrogen dioxide and ozone. Basic cupric nitrate may be formed at the places where the nitrogen dioxide and the ozone concentrations are relatively high. No brochantite was found on the plates in the gas exposure test. The results of regression analysis were very useful to evaluate the levels of complicated air pollution in East Asia.

Key Words East Asia, Acid Deposition, Material Damage, Corrosion Test

1. Introduction

We have found a number of episodic conditions in air pollution due to sulfur oxides emitted from coal fuels in the large cities of China and the other developing countries during our investigations since 1993. These types of air pollution may cause serious damage to materials of cultural and historical artifacts and structures. In the United States and European countries, old statues and monuments even from the Roman days have received serious damage due to acid precipitation or acidic air pollutants in the past 3 decades. A few investigations have been carried out in order to assess the effects of acid rain or acidic air pollution on materials including cultural monuments and structures, and protection measures against such air pollution have been

discussed. However, there have been few basic studies to evaluate the damage, specifically caused by air pollution on materials of cultural and historical artifacts among the various cities in developed and developing countries. Metal, marble, wood and urushi pieces have been exposed to outdoor and indoor airs at 23 sites in China, South Korea and Japan to investigate the relative material damage caused by air pollutants.

There have been few basic studies to evaluate the material damage specifically through experimental corrosion tests conformed to actual environmental situations by using artificial acid rain and complicated acidic gases. We investigated the following three kinds of experimental corrosion tests for copper, (1) an immersion test by nitric acid (HNO₃), hydrochloric acid (HCl) and sulfuric acid (H₂SO₄) solutions, (2) a gas corrosion test by sulfur dioxide (SO₂), nitrogen dioxide (NO₂) and ozone (O₃), and (3) a programmed cyclic corrosion test by using artificial acid rain.

This paper describes the results of atmospheric corrosion test in East Asia and the three kinds of experimental corrosion tests.

2. Atmospheric corrosion test in East Asia

2.1 Methods

Reagents and materials

Acetone and other chemicals were of special grade from Wako (Osaka, Japan). Table 1 indicates the test pieces with their specifications that were exposed to air. Before the exposure, the metallic plates were cleaned with acetone in an ultrasonic bath and the marble piece was cleaned with distilled water in an ultrasonic bath for a few minutes. The test pieces were then dried in a desiccator for 24 hours and weighed. The wooden pieces were dried at 25°C, R.H.59% for 3 days and weighed. The urushi pieces were prepared by Japanese old method.

Table I. Test pieces.

Materials	exposure	size	ingredients	surface
Bronze	unsheltered	2.0 × 30 × 40mm	JIS-H-5111 BC6 Cu85.6%, Sn4.9%, Pb4.9%, Zn4.6%	#400 treatment
Copper	unsheltered rain-sheltered	0.4 × 30 × 40mm	JIS-H-3100 C1201P Cu > 99.9%	#400 treatment
steel	unsheltered rain-sheltered	1.2 × 30 × 40mm	JIS-G-3141 SPPC	#400 treatment
marble	unsheltered rain-sheltered	5.0 × 20 × 20mm	Italian white marble	
cedar	unsheltered	10 × 70 × 70mm	Yoshino sugi	
cypress	unsheltered	10 × 70 × 70mm	Kiso hinoki	
urushi	rain-sheltered	7 × 50 × 50mm	Basic material: straight grained hiba arborvitae (<i>Thujaopsis dolabrata</i>) Uwanuri (the final coat): double coating of roiro urushi (glossy black lacquer)	

Apparatus

A Nippon Test Panel Osaka (Osaka, Japan) exposure panel was used for exposing the test pieces under unsheltered conditions (to outdoor air), and an instrument shelter was used for exposing them under rain-sheltered conditions (to indoor air). A diffusion passive sampler was used for monitoring the concentrations of SO₂ and NO₂ for one-month period. A Nippon Test Panel Osaka (Osaka, Japan) cotton gauze collector was used for trapping the acidic pollutants such as acid fog, acid dew, acidic dust and sea salt. Elionix (Tokyo, Japan) ERAX-3000 scanning electron microscope (with 20 kV, 2,000 times magnifying power) was employed for observing the states of the corrosion products on the samples. A Suga (Tokyo, Japan) UGV-5D gloss meter (reflex angle at 60 degree), a Keyence (Osaka, Japan) VH-6200 digital microscope

(100 times magnifying) were employed for observing the surface states on the samples. A Rigaku (Tokyo, Japan) RINT 1500 X-ray diffractometer (with 40 kV × 150 mA of X-ray power for Cu target) was employed for the qualitative identification of corrosion products. The sulfur and chlorine in the products were determined by using a Rigaku RIX 3000 fluorescence X-ray apparatus. A Nihondenshi (Tokyo, Japan) JEOL 700 with IR-MAU200 microscopic infrared spectrophotometer (measurement range is 25 micrometer in diameter) was employed for the qualitative identification of products in spots on the urushi surface.

Sampling sites and procedure

The 23 sampling sites were situated at the heavily polluted sites in China: (1) Guiyang, (2) Chongqing, (3) Taiyuan; the urban sites in China: (4) Shanghai, (5) Hong Kong, (6) Wuhan, (7) Beijing; the South Korea sites: (8) Taegu, (9) Taejon; the Japan Sea coastal sites: (10) Fukuoka, (11) Toyama, (12) Ishikawa; the urban sites in Japan: (13) Tokyo, (14) Chiba, (15) Osaka (Konohana), (16) Osaka (Higashinari), (17) Nagoya; the rural sites in Japan: (18) Nara, (19) Kyoto, (20) Ibaragi; the chilly sites: (21) Shenyang, (22) Sapporo; the background site: (23) Ichinose. The 7 types of test pieces were exposed to dry and wet deposits under outdoor conditions, and exposed to dry deposits under indoor conditions. The test pieces were collected every 3 months for investigating the short-term impact of acid deposition, and exposed for 1-2 years from 1993 for observing the regional impact on the test pieces at the individual sites.

Monitoring of environmental factors

Temperature, relative humidity (RH), wind direction (WD) and wind velocity (WV) were simultaneously monitored during the exposure using a weather monitoring instrument. The time of wetness (TOW) is defined as period (hrs) when RH was higher than 80 % and temperature was above 0°C. The concentrations of SO₂, NO₂, oxidant (O_x) {or ozone (O₃)} and suspended particulate matter (SPM) {or total suspended particular (TSP)} in ambient air were monitored in the continuous monitoring station at the individual sites. At the sites in China and South Korea where air monitoring systems were not adequately established, the concentration of SO₂ and NO₂ were monitored by the diffusion passive sampler for every one-month period. Sea salt was trapped by using the cotton gauze collector, and determined by ion chromatography (IC). Wet deposits were sampled by using the bulk sampler, and the chemical composition of the deposits was determined by IC.

Microscopic observation and X-ray diffraction analysis

The shapes and the amounts of corrosion, produced on the test pieces after exposure, were observed using the scanning electron microscope. The corrosion products were identified on the metallic plates and the marble pieces by X-ray diffraction analysis.

Determination of sulfur and chlorine

The sulfur and chlorine in the products were determined by using the fluorescence X-ray apparatus.

Determination of corrosion degree

The bronze and copper plates were washed with a 10% ammonium-thioglycolic-acid solution at 80 °C for about 10 minutes to remove the corrosion products. The steel plates were repeatedly washed with a boiling solution of 10% di-ammonium-hydrogen-citrate solution. As for the marble pieces exposed to outdoor air, the pieces were dried in a desiccator for 24 hours without any treatment.

The thickness loss is defined as:

thickness loss (in μm) = 10 × {weight loss (in mg) / surface area (in cm²)} / {specific gravity (in g/cm³)}

Determination on the urushi surfaces

Gross intensities on the urushi surfaces were determined by using the gloss meter. The gloss loss is defined as a percentage of a gross intensity after exposure to one before exposure. The surface state after exposure was observed by using the digital microscope. The products on the surface were identified by using the microscopic infrared spectrophotometer.

2.2 Results and discussion

Environmental factors

The average temperature was 14 – 18 °C at all the sampling sites. The RH was low at the South Korea sites and at the urban sites in Japan. The TOW was more than 4,000 hrs at the Japan Sea coastal sites and at the rural sites in Japan. The WV was about 1 m/sec in the winter at the heavily polluted sites in China. The SO₂ concentration was more than 150 ppb in the winter at the heavily polluted sites in China. However, the NO₂ concentration was relatively high in the urban sites in Japan. The O_X concentration was high in the spring at the Japan Sea coastal sites and at the rural sites in Japan. The TSP concentrations were very high in the spring in China. The amounts of sea salt and rainfall were large in the winter at the Japan Sea coastal sites. The amount of sulfate ion (SO₄²⁻) in the rain was significantly large in the winter at the heavily polluted sites in China.

Microscopic observation

The scanning electron microscopic images of the sample pieces exposed to indoor air for 2 years showed fine crystals of cuprite were formed on the copper plate exposed in Ishikawa, Japan, while green rust covered the plate exposed in Chongqing, China. As for the marble pieces, no changes were observed on the piece exposed in Ibaragi, Japan, while fine crystals like bamboo blades were produced on the piece exposed in Chongqing. The surfaces of the cedar and the cypress plates, exposed to outdoor air, blackened by numerous fine black spots (0.2 mm in diameter). Numerous fine spots (0.2-0.3 mm in diameter) were observed on the surfaces of the urushi plates exposed at Chongqing, China and Taejon, Korea, where dense fog occurred.

Corrosion products

The results of the X-ray diffraction analysis of products on the copper plates and marble pieces showed that basic cupric sulfate, CuSO₄·3Cu(OH)₂ (brochantite), and cuprite, Cu₂O, were qualitatively identified on the copper plate exposed to the outdoor air in Chongqing. At the places where the SO₂ concentration is significantly high, brochantite may be formed on the copper plates. Basic cupric nitrate, Cu(NO₃)₂·3Cu(OH)₂, and cuprite, Cu₂O, were formed on the copper plate exposed to the indoor air in Osaka where the NO₂ concentration was relatively high and the SO₂ concentration is low. As for the results of the marble pieces exposed to the indoor and outdoor airs in Shanghai, China and Osaka, Japan, calcium sulfate, CaSO₄·2H₂O (gypsum), was observed on the pieces exposed to the indoor air at all the sites. No gypsum was found on the pieces exposed to the outdoor air.

Basic lead carbonate, PbCO₃·Pb(OH)₂, was formed on the bronze plates exposed to the outdoor air at the rural sites in Japan. Goethite, lepidocrocite and hematite were formed on the steel plates in Japan, while magnetite was observed on the plates from China after exposure for only 3 months in addition to the above crystals.

Product in the spots on the urushi surfaces

The results of the microscopic infrared spectrometry analysis of products on the urushi surfaces. Carbonyl group qualitatively identified in the spots on the urushi surfaces exposed to indoor air at Chongqing and Taejon. At the places where fog and dew, included the high SO₄²⁻

concentration, were frequently observed, carbonyl groups may be formed on the urushi surfaces. The carbonyl group could be formed by oxidation of a side-chain of urushiol. The first stage of degradation of urushi artifact could be caused by the acidic deposition such as acid fog and dew.

Corrosion degree

The corrosion degree was evaluated by the thickness loss in order to compare the degradation of the 5 types of test pieces. The accuracy on determination of the thickness loss of the copper plates may be proved by 1.2-8.6 % and 0.9-3.4 % of relative standard deviations in the outdoor and indoor exposure in 12 runs (4 times on 3 plates), respectively.

The thickness losses of the samples exposed to the outdoor air were 2-3 times larger than those exposed to the indoor ones. The thickness loss of the steel plate was much higher than those of the other materials. The order of the corrosion degree was steel > marble > bronze > copper. The bronze, used in cultural artifacts and historical structures, was more sensitive to acidic air pollutants than the copper. The copper plate (including the bronze plate) may be very useful for estimating the levels of complicated air pollution for long periods of over 2 years.

Fig. 1 shows that the loss order of the sampling sites from the highest to the lowest was (1) the heavily polluted sites in China (first) > (2) the urban sites in China (second) > (3) the South Korea sites (third) > (4) the Japan Sea coastal sites > (5) the urban sites in Japan > (6) the rural sites in Japan (the lowest). The degree of the thickness loss increased with the concentration of the acidic air pollutants.

Fig. 1. Corrosion rates exposed to outdoor air at the sampling sites.

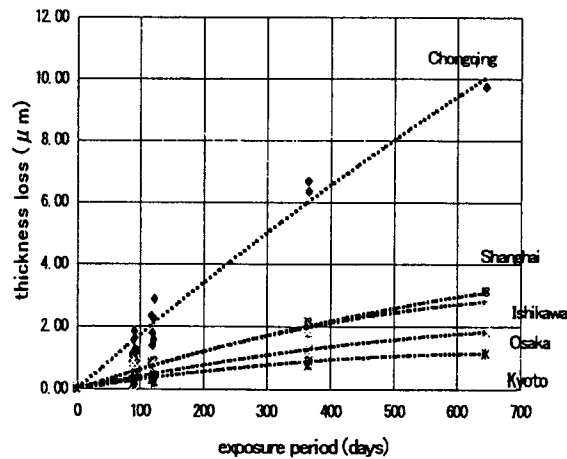
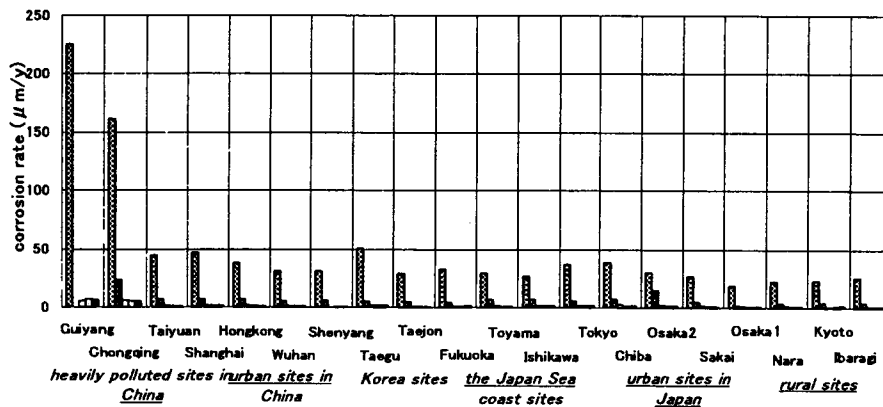


Fig. 2. Thickness losses of bronze exposed to outdoor air vs. exposure period.

As shown in Fig. 2, the corrosion of the bronze plates seemed to be linearly related to the exposure periods in the case of the long-term exposure at all the sites. The corrosion rate of the copper plate (including the bronze plate) may be very useful for estimating the levels of complicated air pollution for long periods of over 2 years.

Environmental factors damaging the materials

Table II shows the results of a regression analysis to estimate the impact of atmospheric components and meteorological conditions on the test piece. The bronze plates, exposed to the outdoor air, were mainly affected by natural phenomena such as meteorological factors and sea salt at the Japanese sites. However, at the Chinese and South Korean sites, the plates were damaged by acidic pollutants such as atmospheric SO₂ and acid rain. The degradation of the marble pieces may be significantly affected by temperature, SO₂ concentration and rainfall, but no degradation occurred due to SO₄²⁻ in the rain. These phenomena are well explained by the Skoulikidis concept that gaseous SO₂ may deposit on the surface of marble and produce gypsum that is washed away with rain water due to the higher solubility than that of CaCO₃ (calcite).

Table II. Results of a regression analysis of material damages and environmental factors.

	the corrosion rate of bronze exposed outdoors(μ m/month)			the corrosion rate of marble(μ m/month)
	in Japan	in China & Korea	total	
observed data	75	23	98	94
multiple correlation coefficient	0.813	0.888	0.852	0.769
variance ratio of F(F-test)	26.8(0.01%>)	23.7(0.01%>)	34.1(0.01%>)	43.3(0.01%>)
regression coefficient (t-test: 5% significant)				
constant	-0.0515	-0.303	-0.170	0.0781
temp($^{\circ}$ C)	0.00460		0.00313	0.0110
RH(%)		0.0101	0.00492	
TOW(hr/month)	0.000135			
WV(m/s)				
SO ₂ (ppb)		0.00184	0.00208	0.00923
NO _x (ppb)				
O ₃ (ppb)	0.00251			
SPM(μ g/m ³)				
sea-salt(μ g/dm ³ /month)	0.0000295		0.0000312	
rainfall(mm/month)				0.00212
pH		-0.0445	-0.0288	
E.C.(μ S/cm)				
SO ₄ ²⁻ (μ g/cm ³)			0.00164	
NO ₃ ⁻ (μ g/cm ³)				
Cl ⁻ (μ g/cm ³)	0.00779		0.00652	

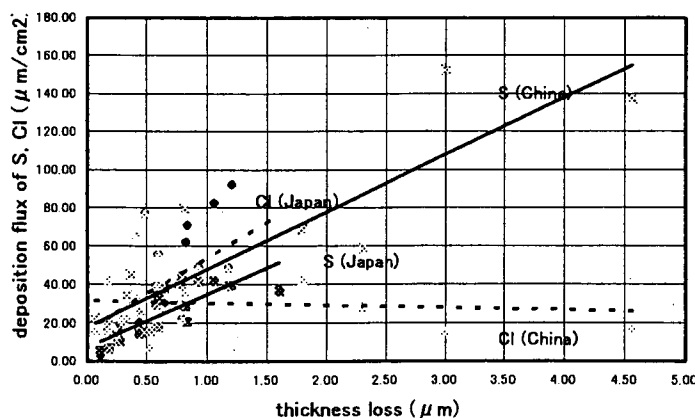


Fig. 3. Relation of the corrosion degree and the deposition flux of S and Cl.

Copper damage and deposition flux of sulfur and chlorine

Fig. 3 shows that the corrosion of the bronze plates exposed to outdoor air was caused by the deposition flux of sulfur (S) and chlorine (Cl). The solid lines indicate the relation between thickness loss and deposition flux of S and dotted lines mean the relation between thickness loss and Cl flux deposited. At the Japanese sites, the corrosion degree of the bronze plates increased with the deposition flux both of S and Cl. However, at the Chinese sites, the corrosion increased with S flux only and was constantly at any deposition flux of Cl.

Table III. Results of a regression analysis of the deposition flux of S and environmental factors.

	outdoor	indoor
	the deposition flux of sulfur on copper (μ g/cm ² /month)	the deposition flux of sulfur on bronze (μ g/cm ² /month)
observed data	53	45
multiple correlation efficient	0.739	0.626
variance ratio of F(F-test)	34.0(0.01% \rightarrow)	8.81(0.01%)
regression coefficient (t-test: 5% significant)		
constant	-8.92	-10.4
temp.($^{\circ}$ C)		
RH(%)	0.152	
TOW(hr/month)		0.0144
WV(m/s)	0.827	2.33
SO(ppb)	0.209	0.950
NO(ppb)		
O ₃ (ppb)		
SPM(μ g/m ³)		
sea-salt(μ g/dm ² /month)		
rainfall(mm/month)	-0.0108	
pH		

Deposition flux of S and environmental factors

Table III shows the relation of the deposition flux of S on the copper plates and the environmental factors derived regression analysis. The regression analysis strongly suggested that gaseous SO₂ could be adsorbed on the wet surface of the copper plates and deposited as a S component on the surface. In the case, little amount of S seemed to be supplied from SO₄²⁻ in rain water. Rain water could wash the S component away from the copper plates, as the regression coefficient of rainfall was of negative value.

3. Experimental corrosion test

3.1 Methods

Reagents, materials and apparatus

Acetone and other chemicals were of special grade from Wako (Osaka, Japan). We used the copper plates (JIS C1201P, 0.3 × 70 × 150 mm, surface area: 210 cm²). Before the exposure, the metallic plates were cleaned with acetone in an ultrasonic bath. The test plates were then dried in a desiccator for 24 hours. After the tests, the copper plates were washed with a 10% ammonium-thioglycolic-acid solution at 80 $^{\circ}$ C for about 10 minutes to remove the corrosion products and dried in a desiccator for 24 hours.

The thickness loss is defined as:

thickness loss (in μm) = $10 \times \{\text{weight loss (in mg)} / \text{surface area (in cm}^2)\} / \{\text{specific gravity (in g/cm}^3)\}$

A Rigaku (Tokyo, Japan) RINT 1500 X-ray diffractometer (with 40 kV \times 150 mA of X-ray power for Cu target) was employed for the qualitative identification of corrosion products.

Immersion test

Three copper plates were immersed in HNO₃, HCl and H₂SO₄, prepared at pH 3.0, 3.5 and 4.0 in order to compare the damages of the various acidic solutions on the copper plates. The acidic solutions were sampled twice times in a month, and the amounts of copper ion in the solutions were determined by inductively coupled plasma (ICP).

Gas corrosion test

A Yamazaki Seiki Kenkyusyo (Kyoto, Japan) MZH-11HS gas corrosion test chamber was used for investigating the effects of SO₂, NO₂ and O₃ on the copper plates. An air stream containing SO₂ (0.1 ppm) and NO₂ (0.1 ppm) were prepared by flushing the SO₂ standard gas (96 ppm in N₂ balance) and NO₂ standard gas (193 ppm in N₂ balance) from Sumitomo-Seika (Osaka, Japan) into the gas corrosion chamber, respectively. The O₃ (0.3 ppm) was prepared by a Yanako (Kyoto, Japan) OZ-2 ozone generator. The experimental conditions were temperature: 20°C \pm 1°C, relative humidity: 90%, exposure period: 5 days, exposure gas: (a) SO₂ (0.1 ppm) + NO₂ (0.1 ppm), (b) SO₂ (0.1 ppm) + NO₂ (0.1 ppm) + O₃ (0.3 ppm).

Programmed cyclic corrosion test by using artificial acid rain

A Suga Weathering (Tokyo, Japan) CCT-1L programmed cyclic corrosion test chamber, using artificial acid rain was used for researching the effects of acid precipitation on the copper plates. Fig. 4 shows the experimental conditions of the programmed cyclic corrosion test.

Table IV. Components of acid precipitation (unit: $\mu\text{g/mL}$)

	pH	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	NH ₄ ⁺	Ca ²⁺	Na ⁺
acid rain in Chongqing	3.15	9.18	4.43	2.05	4.45	9.28	3.80
acid rain in Sakai City	4.20	4.00	5.00	5.00	0.30	0.30	3.50

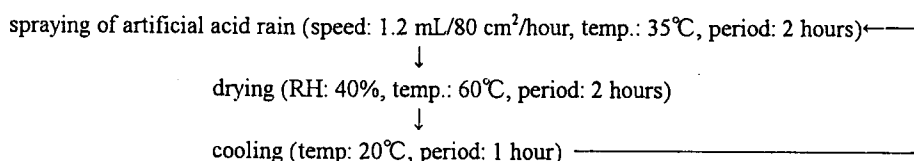


Fig. 4(a). Programmed cyclic corrosion test (c): artificial acid rain was prepared, similar to rain components in Sakai City (see Table IV)

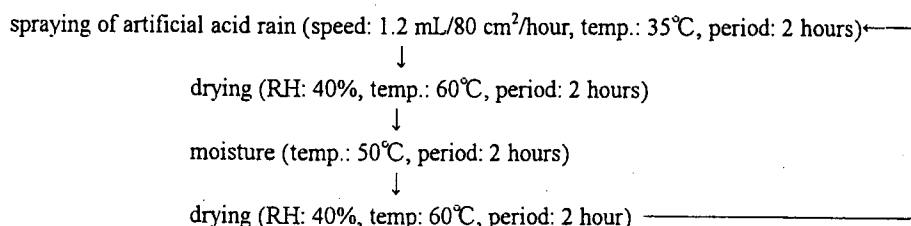


Fig. 4(b). Programmed cyclic corrosion test (d): artificial acid rain was prepared, similar to rain components in Chongqing (see Table IV)

3.2 Results and discussion

Immersion test

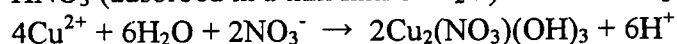
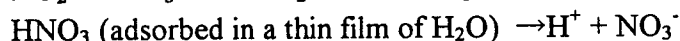
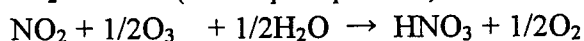
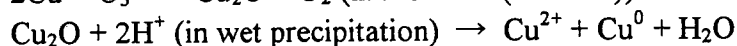
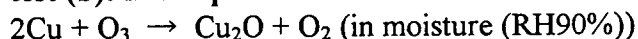
The corrosion degree of the copper plates was significantly large in HNO₃, HCl and H₂SO₄ solutions at pH 3.0 on the initial stage, and decreased with immersed period gradually. The corrosion rate of the copper plates was lower in every acid solutions than the atmospheric corrosion rate in Osaka after the first 60 days of the immersion test. The results of the X-ray diffraction analysis indicated that cuprous oxide (cuprite) was qualitatively identified on the copper plates, immersed in every pH 4.0 acid solution for 30 days. Cuprite and cupric oxide (tenorite), however, were formed on the copper plates immersed in HNO₃ and H₂SO₄, included acetic acid.

Gas corrosion test

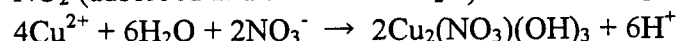
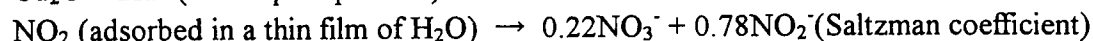
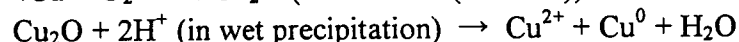
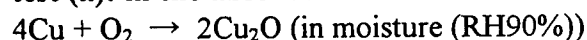
The X-ray diffraction analysis showed that cuprite and basic cupric nitrate were formed on the copper plates under the gas corrosion test in the presence of ozone (b) or in the absence of ozone (a). Basic cupric nitrate seemed to be formed on the copper plates at the places where the NO₂ concentration was relatively high.

basic cupric nitrate formation

test (b): in the presence of ozone

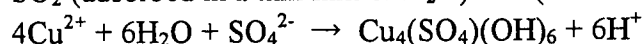
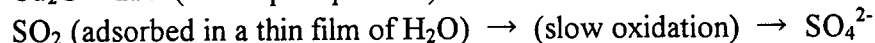
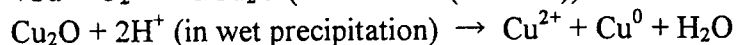
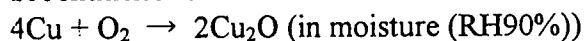


test (a): in the absence of ozone



No brochantite was formed on the copper plate. The exposure period of 5 days could be too short to produce SO₄²⁻ in a thin film of H₂O on the copper plate.

brochantite formation



Programmed cyclic corrosion test by using artificial acid rain

The results of the programmed cyclic corrosion test are shown in table V. The corrosion rate increased with pH value negatively under both of the cyclic corrosion test (c) and (d). In the case of pH 4.0, the test (d), 3.65 μ m/year indicated 8 times larger than the test (c), 0.44 μ m/year. The rain in Sakai City included nitrate ion, 5.00 μ g/mL and chloric ion, 5.00 μ g/mL, and the rain in Chongqing involved sulfate ion, 9.18 μ g/mL, ammonium ion, 4.45 μ g/mL and calcium ion, 3.80 μ g/mL. However, the effect of such ions on the copper corrosion may be low due to a little amount of every ion in the rains. The difference between the test (c) and the test (d) may be caused mainly by the moisture cycle in the test (d). The X-ray diffraction analysis indicated that cuprite and tenorite (in partial) were formed on the copper plates under the

programmed cyclic corrosion test. No basic cupric nitrate and brochantite were found on the plates under the corrosion test. The amounts of H^+ and SO_4^{2-} in the artificial acid rain of Chongqing may be too little to produce brochantite on the copper plates.

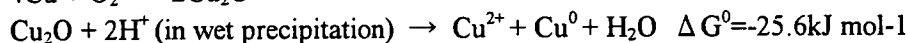
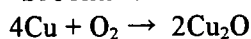
Table V (a). The results of the programmed cyclic corrosion test (c).

	exposure period	corrosion rate
pH 3.0	24 cycles (5 days)	2.77 μ m/year
pH 4.0	24 cycles (5 days)	0.44 μ m/year

Table V (b). The results of the programmed cyclic corrosion test (d).

	exposure period	corrosion rate
pH 3.0	15 cycles (5 days)	5.48 μ m/year
pH 4.0	15 cycles (5 days)	3.65 μ m/year
pH 4.5	15 cycles (5 days)	1.02 μ m/year

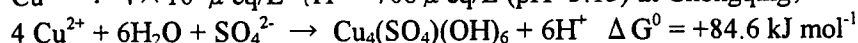
brochantite formation in the programmed cyclic corrosion test



$$-(\Delta G^0/RT) = \ln([Cu^{2+}]/[H^+]^2)$$

$$[Cu^{2+}]/[H^+]^2 = 8 \times 10^4$$

$$Cu^{2+} \cong 4 \times 10^4 \mu \text{ eq/L} \quad \{H^+ = 708 \mu \text{ eq/L (pH=3.15) at Chongqing}\}$$



$$[H^+]^6 / ([Cu^{2+}]^4 [SO_4^{2-}]) \leq 2 \times 10^{-17}$$

$$[H^+]^6 / ([Cu^{2+}]^4 [SO_4^{2-}]) \cong 2.6 \times 10^{-10} \quad \{SO_4^{2-} = 191 \mu \text{ eq/L (9.18 } \mu \text{ g/mL) at Chongqing}\}$$

4. Conclusions

The results of the atmospheric corrosion test suggest that the corrosion rates of the copper samples are useful for monitoring the qualitative and quantitative acid depositions over a long-term period. The type of corrosion was characterized on steel, copper and marble pieces by type and concentration of air pollutants. Of the air pollutants, SO_2 is significantly destructive to metallic and marble materials composing cultural and/or historical artifacts. The results of the experimental corrosion test indicate that cuprite and tenorite (in partial) were formed on the copper plates under the immersion test and the programmed cyclic corrosion test. No basic cupric nitrate and brochantite were found on the plates. Cuprite and basic cupric nitrate, however, were formed on the copper plates under the gas corrosion test in both cases of ozone presence and not. Basic cupric nitrate seemed to be formed on the copper plates at the places where the NO_2 concentration was relatively high. The results strongly suggested that a new technology, combined the gas corrosion test with the programmed cyclic corrosion test, could be developed in order to simulate actual environmental situations. The results of regression analysis were very useful to evaluate the levels of complicated air pollution in East Asia.