Development of Copper Corrosion Products and Relation between Surface Appearance and Corrosion Rate

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Copper was exposed unsheltered and sheltered in four humid tropical sites, representing urban, urban-industrial, urban-marine and rural environments. The corrosion rates and the sequence of corrosion product formation are presented and discussed in relation with climatic and atmospheric pollution parameters. Chemical compositions of corrosion products were found to depend on environments and duration of exposure. In all environments, cuprite was the predominating corrosion product that formed first and continuously increased during the exposure. Among the sulphur-containing corrosion products, posnjakite and brochantite were more frequently found and the first formed earlier. Nantokite was the most common chlorine-containing products for most cases, except the high-chloride environment, where atacamite was detected instead. The corrosion rate of copper was well indicated by the colour of patina. The red-purple colour corresponded to the high corrosion rate and the greenish grey colour corresponded to the low corrosion rate. Corrosion rate of sheltered copper in urban-marine environment increased with the exposure time.

Keywords : *copper corrosion, corrosion product, corrosion rate, brochantite, nantokite.*

1. Introduction

Copper has long been a traditional material for sculptors, monuments, roofs and goods in different parts of the world. And it was the first metal that ancestors produced and used for making tools, weapons and home-hold goods. Until now copper and its alloys are the most important material used in different industries. For this reason, atmospheric corrosion of copper is a subject of great importance for material development and application. A special attention has been paid for a copper corrosion in humid tropical countries due to its specific climate with high temperature, high humidity, prolonged rain and long time of wetness. Corrosion of copper became more severe for the areas with high concentration of chloride aerosols and other industrial corrosive pollutants like south of Vietnam. There are numerous publications concerning corrosion of copper around the world; however there is very few information about copper corrosion in Vietnam. This research attempts to characterize corrosion behaviour of cop-

per in the humid tropical environment with considering influences of atmospheric pollution parameters. Long term field exposure results of copper at four climatic sites of South Vietnam since 2001 have been reported in the point of corrosion rate and sequence of corrosion product formation.

2. Experiment

Copper with chemical composition given in Table 1 has been tested under unsheltered and sheltered conditions at four sites in an exposure campaign from July 2001 to January 2007. The climatic factors such as temperature, relative humidity, rainfall and number of rainy days were obtained from the meteorological stations where the exposure was conducted. Chloride aerosols and sulphur dioxide, nitrogen oxide in the air were determined by dry gauze and passive sampling methods once a month. The locations and average values of environmental characteristics of the four sites are described in Table 2. The environment at HoChiMinh City and Bien Hoa is sulphur dominating, while that at My Tho and Vung Tau is chloride domina-

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Table 1. Composition of Copper Sample

Element	Cu	Al	Fe	Cl	Si	Ca	S	Ni
Composition (%)	99.6	0.193	0.0893	0.0459	0.0354	0.0338	0.0225	0.0136

Table 2. Environmental characteristics of the testing sites

Parameter / Site	Bien Hoa	Vung Tau	HoChiMinh City	My Tho
Classification	Urban	Urban-marine	Urban-Industrial	Rural
Latitude/longitude	10^o57N; 106^o51E	10^o21N; 107^o05E	10^o49N; 106^o40E	$10^o22'N$; $106^o24'E$
Distance from the sea, *km*	55	2.00	~ 47.0	45
Altitude, *m*	15.6	4.0	4.6	1.1
Average temperature, ℃	27.6	27.4	28.3	26.9
Average humidity, *%*	78	79	74	82
Time of wetness, *h/year*	4220	4660	3210	4940
Total rainfall, *mm/year*	1813	1322	1522	1207
Number of rainy day (days/year)	140	106	135	125
Cl^-, $mg/m^2.d$ (unsheltered)	2.0	11.2	3.3	4.8
Cl^-, $mg/m^2.d$ (sheltered)	0.45	2.6	3.3	0.71
SO_2, $\mu g/m^3$	24	8	42	7
NO_2, $\mu g/m^3$	25	11	12	22

ting. It should be emphasized that at Vung Tau and My Tho there was very big variation in monthly airborne salinity. The airborne salinity in dry season was very high, especially at Vung Tau.

The specimens were mounted on the exposure racks by polycarbonate bolts at an exposure angle of 45° facing south under the unsheltered condition, and hang up freely by nylon lines under the sheltered condition. For studying seasonal and pollution effect on corrosion, a short-term three-month exposure was conducted in addition with long-term exposure. In South Vietnam a year is divided into dry and rainy seasons. Rainy season begins in the end of May and ends in the end of November. In present research three-month periods are as follows: January-March (Q1), April-June (Q2), July-September (Q3), and October-December (Q4). Rainfall at the four sites is in the order Q3> Q2≅ Q4. Period January-March has no rain and is termed as an absolute dry period. The relative humidity at the four sites is in the same order as the rainfall. The airborne salinity in Q1-Q2 periods normally were higher than Q3-Q4 periods with the highest airborne salinity of Q1 period. This related to monsoons blowing from the sea to the land (east winds), a penetration of seawater into river mouths and an absent of rains in dry season. This phenomenon was the most pronounced at Vung Tau and My Tho.

The treatment of copper specimens before and after exposure was conducted according to standards. Crystalline phases of corrosion products were identified by X-RAY diffraction method. In addition, Fourier transform infrared reflection absorption spectroscopy (IR-RAS) was applied to examine non-crystalline corrosion products. The corrosion rates C_R and the thickness losses T_L were estimated as follows:

$$T_L \ (\mu m) = 10 \ \text{mass loss} \ (mg/cm^2)/\text{density} \ (g/cm^3) \qquad (1)$$

$$C_R \ (\mu m/year) = T_L \ (\mu m)/\text{duration of the exposure (year)} \quad (2)$$

where the density of copper was assigned to 8.92 g/cm^3. The mass gains, mass losses, thickness losses, and corrosion rates were estimated as the average ones of the duplicated identical specimens. The kinetic of copper corrosion was evaluated based on an equation $T_L = At^b$, were T_L (μm) is the thickness loss after t-year exposure, A is the corrosion rate after one-year exposure and exponent b is a measure of protection ability of corrosion layer.[1] The kinetic of copper corrosion was evaluated in the relation with the environmental factors such as SO_2 concentrations, airborne salinity, relative humidity, and rainfall⋯ Also, the mass gain/mass loss ratios were evaluated in term of rainfall and pollution level at the sites.

3. Results

3.1 Visual appearance of the copper specimens after exposure

Specimens exposed to different environments showed different visual appearances. The two sides of sheltered specimens were almost the same, while the skyward and groundward sides of unsheltered specimens looked different.

3.1.1 Sheltered specimens

The sheltered specimens exposed in the sulphur-dominating environments at HoChiMinh and Bien Hoa in initial stage of exposure had brownish colour, which became darker and turned to red-brown and then-dark brown during the exposure. On the contrary, the 3-month sheltered specimens of chloride-dominating environment at My Tho and Vung Tau were heterogeneous in colour with the salmon-pink or red stains on the brownish surface. They became purple or red-purple as the exposure was more than one year. Especially, the copper patina at Vung Tau appeared poor adherent to the background. There, the salmon-pink stains were easily removed by a light scratching.

3.1.2 Unsheltered specimens

The unsheltered specimens at HoChiMinh and Bien Hoa after 3-month exposure were brownish with brown spots that became darker and larger during the exposure. They turned to greenish-grey after 1- or 2-year exposure. The skyward side was always darker than the groundward side. The unsheltered specimens exposed at Vung Tau were coloured to red-purple or red-brown. There the groundward side of the 3-month specimens exposed in rainy periods showed stronger red tone than the skyward ones, but the reverse was observed for dry periods. The red-purple patina formed at Vung Tau was porous and poor adherent to the background. It exfoliated and peeled of with long exposure, revealing a green layer underneath. The skyward side showed exfoliation when the exposure was about 1 year, while the groundward side showed the exfoliation much later. The exfoliation of copper patina was characterized for Vung Tau only. The unsheltered specimens at My Tho exposed in 3-month periods with the high airborne salinity (Q) 1were purple coloured like most of the specimens at Vung Tau. However the specimens exposed in 3-month periods with the low airborne salinity (Q3) were brownish, but changed to red-brown, then greenish-grey with prolonged exposure like the specimens at HoChiMinh and Bien Hoa. The formations of greenish-grey layer on the unsheltered specimens at My Tho, HoChiMinh, and Bien Hoa were similar. There, the greenish layer developed on the top of corrosion layer previously formed, while at Vung Tau, the green layer was formed under the

purple layer and caused the cracking and exfoliation of the top layer.

3.2 Corrosion rate of the specimens

Fig. 1 shows the corrosion rates of sheltered and unsheltered copper at the four sites. Overall, the corrosion rates of unsheltered copper were much higher than those of sheltered copper exposed in the same period at the same site. Moreover, the corrosion rate at Vung Tau was much higher than the corrosion rates at the other sites both under sheltered and unsheltered conditions.

3.2.1 Sheltered Specimens

Corrosion rates under sheltered condition were in the order of Bien Hoa < HoChiMinh ≈ My Tho << Vung Tau for any duration of exposure. They decreased during exposure at HoChiMinh, My Tho, and Bien Hoa, but increased along with exposure at urban-marine site Vung Tau. Season clearly influences on corrosion rate. The corrosion rates of the 3-month sheltered specimens were higher in the Q1-Q2 periods than in the Q3-Q4 periods. This was strongly pronounced in chloride dominating environment at My Tho and Vung Tau.
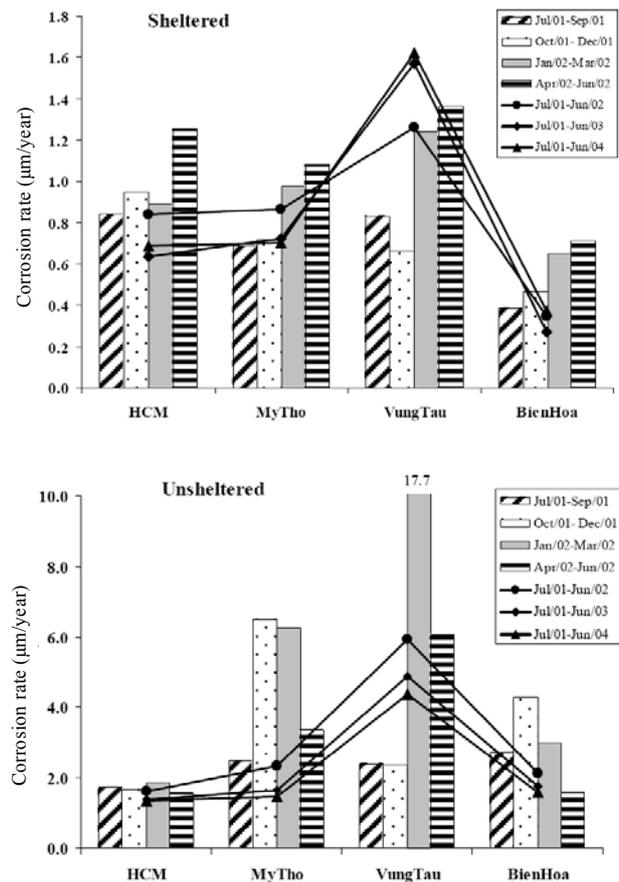

Fig. 1. Corrosion rate of the copper specimens at four sites.

3.2.2 Unsheltered specimens

The corrosion rates of the unsheltered copper were in the order HoChiMinh < My Tho < Bien Hoa << Vung Tau with a little difference between those at HoChiMinh, My Tho and Bien Hoa. In addition, they gradually decreased during exposure at any site. The seasonal effect on corrosion rate of unsheltered copper appeared inconsistent at the four sites. It was strongly pronounced at Vung Tau and My Tho, where the corrosion rates of the 3-month specimens were the lowest in the heavy-rainy period from July to September. At My Tho, they became almost twice in periods from October to March. At Vung Tau, they were extremely high in dry season, about 2.5 - 6 times higher than those observed in rainy periods. At Bien Hoa, the corrosion rate of the 3-month specimens was the highest in the transition period from rainy to dry season (Q4), and the lowest in the transition period from dry to rainy season (Q2). In contrary, no remarkable seasonal variation in the corrosion rates was seen at HoChiMinh. All the above mentioned was observed and for the three-month specimens of any year in the exposure campaign.

3.3 Time dependence of thickness losses

Fig. 2 show the thickness losses of the sheltered and unsheltered copper at the four sites versus the duration of the exposure, where the 3-month thickness losses were estimated as the average ones of the four 3-month thickness losses in a year.

The A and b values obtained by applying the equation $T_L = A \times t^b$ are given in Fig. 3. The b value was close to 1 for unsheltered copper at HoChiMinh (almost unchanged corrosion rate with time), and 1.2 for sheltered copper at Vung Tau (increasing corrosion rate with time). The b value of about 0.5 was observed for unsheltered copper at My Tho (corrosion rate is strongly suppressed with
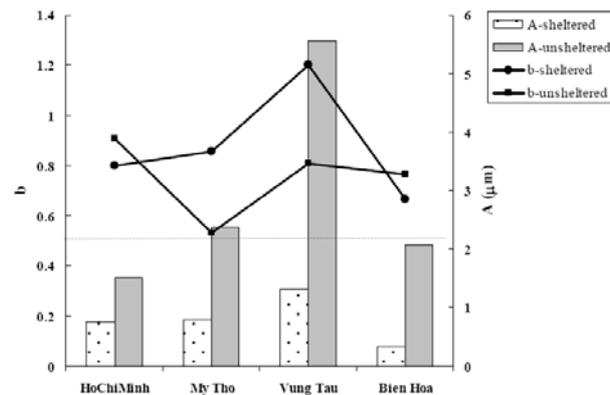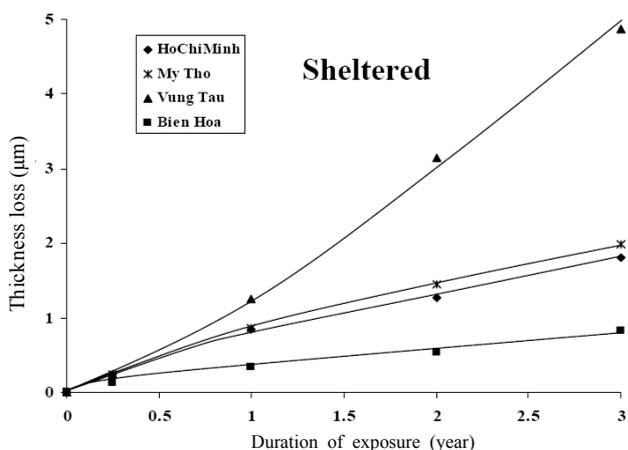

Fig. 3. Site dependence of b value (the lines, the left axis) and A value (the columns, the right axis) for the corrosion rates of copper at the four sites.

time). For the other cases b value was in the range 0.7-0.8.

3.4 Mass gains and mass losses of the copper specimens

The mass gain/mass loss ratios of the copper specimens are given in Fig. 4, where the dash lines represent theoretical ratio mass gain/mass loss of cuprite Cu_2O and brochantite $Cu_4(SO_4)(OH)_6$. They were largely different under unsheltered and sheltered conditions, changed with the duration of the exposure and varied largely depending on season. For the sheltered specimens, they increased with increasing of the SO_2 concentration in the air at the sites. For the unsheltered specimens, they were very low and decreased with time, especially at Vung Tau.

3.5 Corrosion products of sheltered and unsheltered copper

Considering that the visual appearances were similar for the two sides of the sheltered specimens, but different for the unsheltered ones, the corrosion products on the two
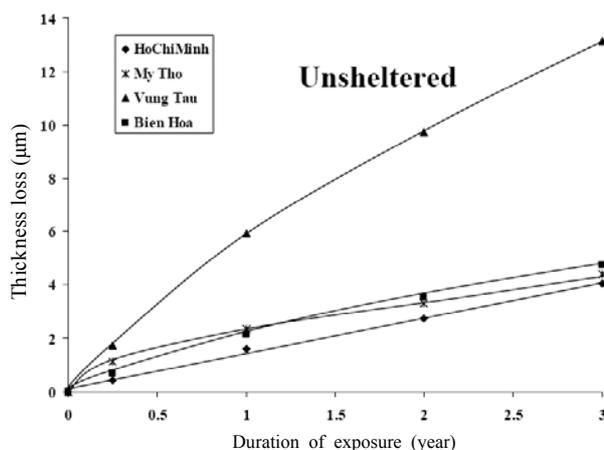

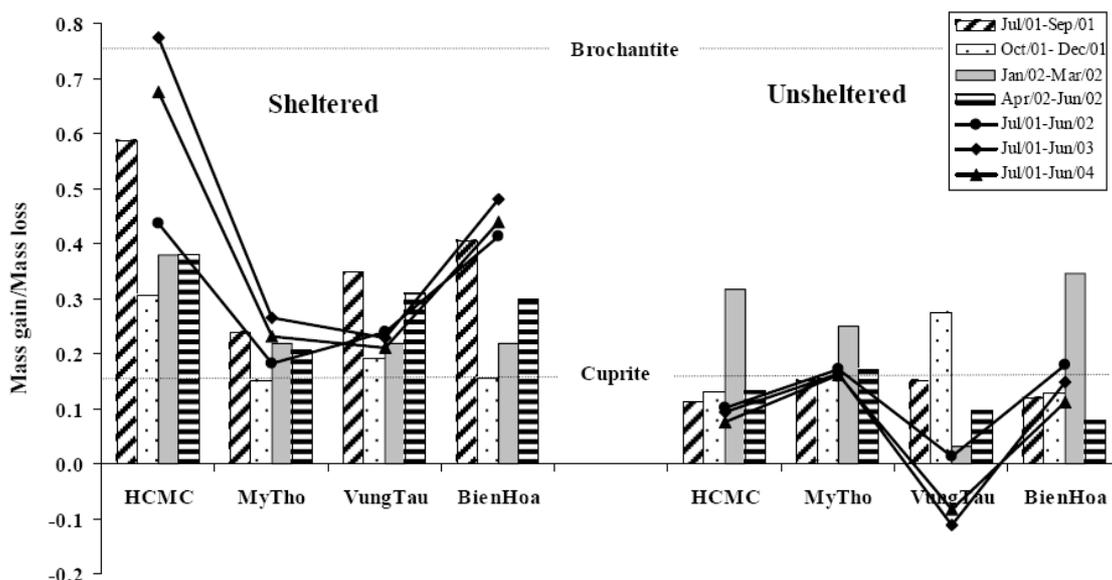**Fig. 2.** Time dependence of the thickness losses of copper at the four sites.

Fig. 4. Mass gain/mass loss ratios of sheltered and unsheltered specimens at four sites.

sides of specimens were assumed to be identical under sheltered, but different under unsheltered conditions. Therefore, XRD and IR-RAS analysis were conducted for a one side of the sheltered specimens, but for both sides of the unsheltered specimens. The components of corrosion products were found depended on the duration of exposure as well as on the sites, and were different on the two sides of unsheltered specimens.

3.5.1 Intermediate Non-Crystalline products

Fig 5 gives representative IR-RAS spectrum of corrosion layers on the 3-month sheltered specimens at HoChiMinh. IR-RAS method enables determination of intermediate non-crystalline corrosion products that are not able to be detected by XRD method.

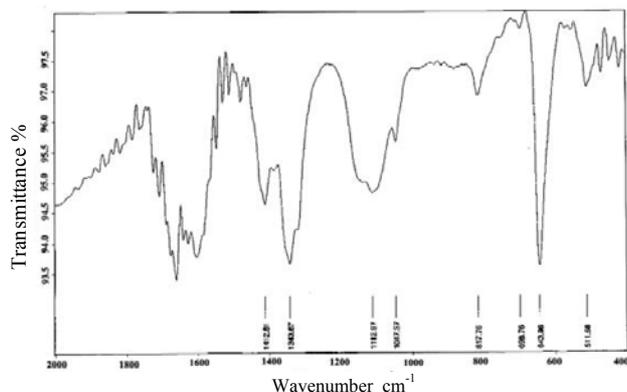According to Leygraf *et al.*, an IR-RAS peak around

Fig. 5. Representative IR-RAS spectrum of the corrosion layers on the 3-month sheltered specimens at HoChiMinh.

1107 cm^{-1} is assumed to be a sign of cupric sulphate (CuSO$_4$), while splitting of the peaks into two peaks at around 1070 and 1120 cm^{-1} is a sign of a basic copper sulphate.[2)-6)] The peaks around 1420 and 1350 cm^{-1} were considered to characterize nitrate compounds, and a peak at around 650 cm^{-1} is evidence of Cu$_2$O. In this study, the peak of cupric sulphate at 1110 cm^{-1} was common for all specimens, although the peaks at 1120 cm^{-1} and 1070 cm^{-1} were observed for not all of them. On the contrary, the IR-RAS peaks of nitrates were not found at all for the specimens at Vung Tau and My Tho regardless of exposure methods. Nonetheless, for the specimens at Bien Hoa and HoChiMinh they were detected for the sheltered specimens, unsheltered specimens of the absolute dry periods, and the groundward side of very few unsheltered ones. Thus, basic copper sulphate could form only in some cases, but the intermediate copper sulphate was characterized for all specimens in any environments. However, the formation of copper nitrates was possible only in the environments highly polluted by NO$_2$ such as HoChiMinh and Bien Hoa, but once formed it was washed off by rain from unsheltered copper due to its high solubility.

Figs. 6-7 show representative XRD patterns of the corrosion products on copper specimens at four sites, where 3-month, 1year, and 2-year exposure periods were designated as 3M, 1Y, and 2Y, respectively. "S" and "G" indicate skyward and groundward sides of unsheltered specimens. Dry and rainy season are denoted as D and R. The sites were symbolized by HCM (HoChiMinh), MT (My Tho), VT (Vung Tau), and BH (Bien Hoa). As HCM 3M S R indicates a skyward side of a specimen exposed

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Table 3. Corrosion Products of Sheltered Copper

	Corrosion product	Cuprite	Langite	Posnja kite	Brochan tite	Copper hydroxide	Nanto kite	Ataca mite
HoChiMinh	3-month dry season	major		minor			trace	
	3-month rainy season	major		trace				
	1-year	major		minor			minor	
	2-year	major		minor	trace		minor	
My Tho	3-month dry season	major		trace				
	3-month rainy season	major						
	1-year	major		trace	minor	trace	trace	
	2-year	major		trace	minor	trace		
Vung Tau	3-month dry season	major		minor				
	3-month rainy season	major		minor				
	1-year	major	trace	minor	trace	trace		
	2-year	major	trace	minor	trace	trace		trace
Bien Hoa	3-month dry season	major		trace				
	3-month rainy season	major		trace				
	1-year	major		minor		trace	trace	
	2-year	major		minor		trace	minor	

three months in rainy period at HoChiMinh. The corrosion products found were cuprite Cu_2O, copper hydroxide $Cu(OH)_2$, langite $Cu_4(SO_4)(OH)_6 \cdot 2H_2O$, posnjakite $Cu_4(SO_4)(OH)_6 \cdot H_2O$, brochantite-M $Cu_4(SO_4)(OH)_6$, nantokite $CuCl$, atacamite $Cu_2Cl(OH)_3$ and botallackite $Cu_2Cl(OH)_3$ (an isomorphous form of atacamite). In some cases, copper patina contained substances not related with copper such as quartz (SiO_2), gypsum $(CaSO_4 \cdot 2H_2O)$ and other minerals like $K(Na)Al_xSi_yAl_zO_t(OH)_2$ or $xCaO \cdot ySiO_2 \cdot zH_2O$. The constituents of corrosion products are summarized in Tables 3 - 4.

The composition of corrosion products under unsheltered conditions was more complex then under sheltered conditions. Nevertheless cuprite was always the preliminary corrosion product that increased during exposure regardless of exposure method and environment. The constituent of copper patina became more complex with prolong exposure, and its complexity depended on environments and exposure time.

3.5.2 Cuprite

Cuprite was always predominant in corrosion layers. Commonly, the amount of cuprite was much higher on the skyward side than on the groundward side for the unsheltered specimens at four sites. An exception was a few 3-month specimens at My Tho and Vung Tau exposed in the absolute dry period.

3.5.3 Brochantite

It is well known that brochantite is the most important product of copper corrosion owing to its high protection ability, and since it is the most frequent corrosion product of copper.

Sheltered specimens - Brochantite was not found on any sheltered 3-month specimens at all. It was abundant on the specimens at My Tho and in small amounts at Vung Tau as the time of exposure was one year. In the surprise, the formation of brochantite appeared to be delayed at sulphur dominating environments at HoChiMinh and Bien Hoa. A trace amount of brochantite was detected on the 2-year specimens at HoChiMinh, but it was not found on any sheltered specimens at Bien Hoa even after 2-year exposure. The observed was in the opposite of the expected that brochantite would form faster in a sulphur-dominating environment.

Unsheltered specimens - In non-marine environment (HoChiMinh, My Tho, Bien Hoa) brochantite did not form on 3month specimens exposed in rainy season, but it was detected on the 3-month specimens exposed in the absolute dry period and on all the 1-year specimens. In urban-marine site at Vung Tau, brochantite was found as a trace only on the skyward side of the 2-year specimens. Thus, chloride hinders the formation of brochantite. However, it was figured out from the peak intensity of brochantite at d = 6.375 Å and d = 3.898 Å that the growth of brochantite was the highest at Bien Hoa, followed by that at My

Table 4. Corrosion Products of Unsheltered Copper

	Corrosion product		Cuprite	Langite	Posnjakite	Brochantite	Copper hydroxide	Nantokite	Botallackite	Atacamite
HoChiMinh	3-month dry season	S. side	major		minor	trace		trace		
		G. side	major		minor			trace		
	3-month rainy season	S. side	major		oc					
		G. side	major							
	1-year	S. side	major		trace	trace		trace		
		G. side	major		minor			minor		
	2-year	S. side	major		trace	minor				
		G. side	major		minor			minor		trace
My Tho	3-month dry season	S. side	major		minor	oc		minor		
		G. side	major					minor		
	3-month rainy season	S. side	major	trace	oc					
		G. side	major		oc					
	1-year	S. side	major	trace	minor	trace		minor		trace
		G. side	major		minor	minor	trace	minor		
	2-year	S. side	major	trace	trace	minor		minor		trace
		G. side	major		trace	minor	trace	minor		
Vung Tau	3-month dry season	S. side	major							trace
		G. side	major							trace
	3-month rainy season	S. side	major		trace			oc		
		G. side	major		trace			oc		
	1-year	S. side	major		trace					minor
		G. side	major					oc		minor
	2-year	S. side	major		trace	trace			trace	minor
		G. side	major							minor
Bien Hoa	3-month dry season	S. side	major		trace	trace		trace		
		G. side	major		trace			trace		
	3-month rainy season	S. side	major		trace	oc				
		G. side	major		trace	oc				
	1-year	S. side	major	trace	trace	minor				
		G. side	major		trace	minor		minor		
	2-year	S. side	major	trace	trace	minor				
		G. side	major		trace	minor	trace	minor		

*oc: occasionally

Tho, and then finally at HoChiMinh. Thus, the growth of brochantite was found not to associate with the concentration of SO₂ in the air. Also, the formation of brochantite at HoChiMinh, My Tho, and Bien Hoa under the unsheltered condition occurred earlier than under sheltered condition.

3.5.4 Atacamite and Botallackite

Atacamite was clearly showed in the XRD patterns of the 3-month unsheltered specimens at urban- marine site Vung Tau, and increased during exposure. It was also detected in trace level on the 2-year unsheltered specimens at HoChiMinh and My Tho, and 2-year sheltered specimens at Vung Tau. Botallackite - an isomorphous compound of atacamite was detected only on the skyward side of the 2-year unsheltered specimens at Vung Tau.

3.5.5 Nantokite

Nantokite was the most fairly frequent chlorine-containing product found in rural, urban, and urban-industrial site. There, nantokite was detected on the 3-month unsheltered specimens exposed in dry period and one-year and 2-year sheltered and unsheltered specimens; although under unsheltered condition it was more frequently found on the groundward side. In addition, nantokite increased gradually with extending exposure. On the contrary, in urban-marine site Vung Tau nantokite was detected on the 1, 2 -year sheltered specimens. Under unsheltered condition at Vung Tau it was found as a trace on very few 3-month specimens exposed in rainy season but disappeared afterward.
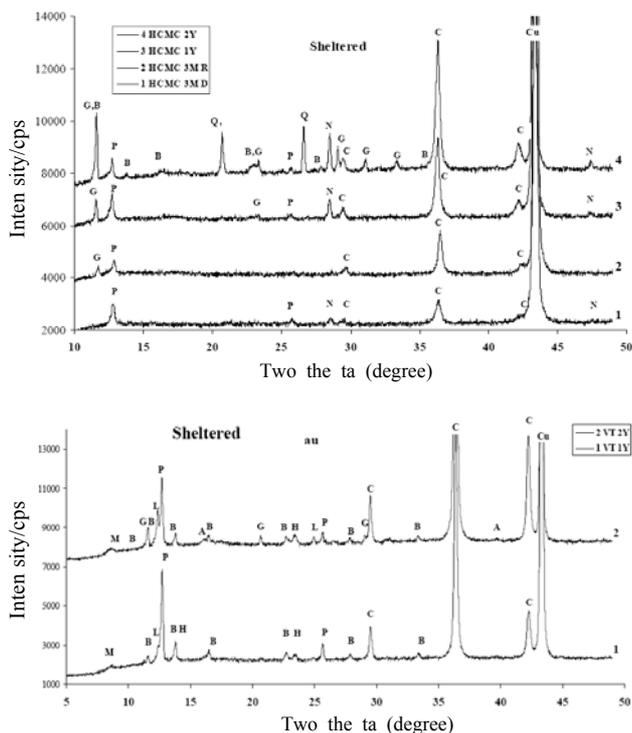
Fig. 6. XRD patterns of the sheltered specimens at HoChiMinh (HCMC) and Vung Tau (VT). Cuprite Cu_2O (C), copper (II) hydroxide $Cu(OH)_2$ (H), brochantite-M $Cu_4(SO_4)(OH)_6$ (B), posnjakite $Cu_4(SO_4)(OH)_6 \cdot H_2O$ (P), langite $Cu_4(SO_4)(OH)_6 \cdot 2H_2O$ (L), nantokite $CuCl$ (N), atacamite $Cu_2Cl(OH)_3$ (A), botallackite $Cu_2Cl(OH)_3$ (D), gypsum $CaSO_4 \cdot 2H_2O$ (D), quartz SiO_2 (Q), and $K(Na)Al_xSi_yAl_zO_t(OH)_2$ or $xCaO \cdot ySiO_2 \cdot zH_2O$ (M).

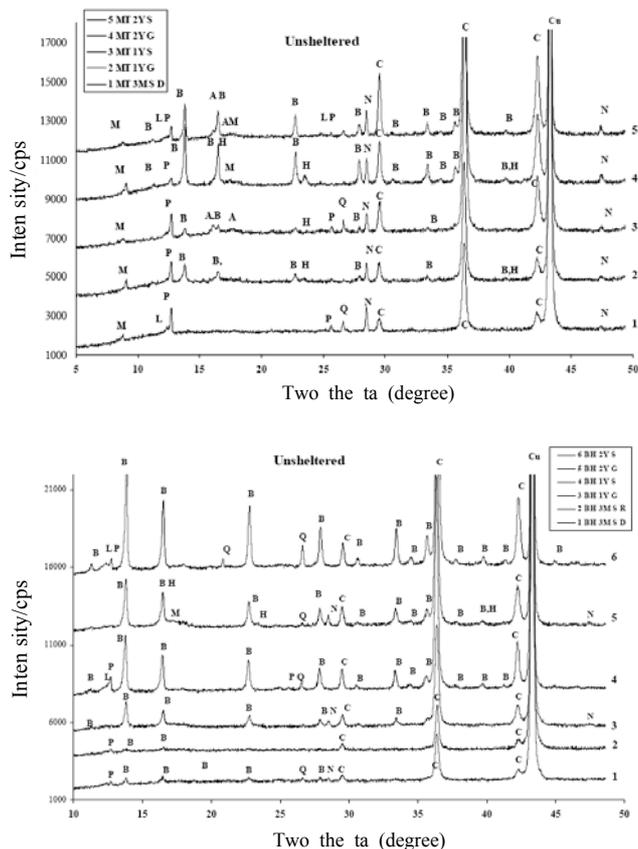**Fig. 7.** XRD patterns of the unsheltered specimens at My Tho (MT) and Bien Hoa (BH). Cuprite Cu_2O (C), copper (II) hydroxide $Cu(OH)_2$ (H), brochantite-M $Cu_4(SO_4)(OH)_6$ (B), posnjakite $Cu_4(SO_4)(OH)_6 \cdot H_2O$ (P), langite $Cu_4(SO_4)(OH)_6 \cdot 2H_2O$ (L), nantokite $CuCl$ (N), atacamite $Cu_2Cl(OH)_3$ (A), botallackite $Cu_2Cl(OH)_3$ (D), gypsum $CaSO_4 \cdot 2H_2O$ (D), quartz SiO_2 (Q), and $K(Na)Al_xSi_yAl_zO_t(OH)_2$ or $xCaO \cdot ySiO_2 \cdot zH_2O$ (M).

3.5.6 Copper hydroxide

copper hydroxide was found on the groundward side of the unsheltered specimens at My Tho and Bien Hoa, and on the 1-year sheltered specimens at My Tho, Vung Tau, and Bien Hoa. It was not detected in high-SO_2 environment at HoChiMinh.

3.5.7 Langite and posnjakite

Langite was found on some specimens at My Tho, Vung Tau and Bien Hoa but not found at HoChiMinh at all. The observed more or less was in accordance with the reported in some papers that langite was considered as a precursor of brochantite in low-sulphur environment.[1),2),7)-13)] Concerning posnjakite, we should pause upon clarifying it's presence. The XRD diffractions at d = 6.95Å and d = 3.47Å were found frequently on XRD patterns of the sheltered and unsheltered specimens. They can be assigned to posnjakite as well as copper basic nitrate $Cu_2NO_3(OH)_3$ (JCPDS- monoclinic, Card No. 450594). Posnjakite has two diffractions at d = 6.95Å and d = 3.48Å that are similar to those of copper basic nitrate at d = 6.94Å and d = 3.47Å. However, from the IR-RAS analyses, the ex-

istence of copper nitrate substances was possible only on sheltered specimens and the groundward side of unsheltered specimens at HoChiMinh and Bien Hoa. Therefore, the formation of basic copper sulphate was considered more potential. Hence, the XRD diffractions at d = 6.94Å and d = 3.47Å were assigned to posnjakite. However, it was possible that copper basic nitrate might form on sheltered copper specimens protected of rain at HoChiMinh and Bien Hoa. From Table 3-4 posnjakite formed on 3-month specimens in any environment, much earlier than brochantite. Commonly, the intensity of the diffractions of posnjakite increased in the initial stage of exposure; but in some cases it decreased afterward along with increase of the intensity of XRD diffractions of brochantite as in the case of unsheltered specimens at My Tho and Bien Hoa, and sheltered specimens at HoChiMinh, My Tho, and Vung Tau. The observed was in agree with the results reported in some papers that posnjakite trans-

forms into brochantite and tends to be lost after long exposure.

4. Discussions

4.1 Effects of environmental factors on corrosion rate of copper

4.1.1 Sheltered specimens

The corrosion rate of sheltered copper at Vung Tau was very high (1.8 µm/year) and increased with time, while those at the other sites were 0.3-0.8 µm/year and decreased with time. The reported data of copper corrosion under sheltered condition is scarce. Anyway, the corrosion rate of 0.8 µm/year was much higher than the frequent observed corrosion rate in Japan and China, but comparable with those in tropical Cuba. The corrosion rate at Vung Tau was similar to those of highly-polluted sites in China, but less than those of coastal sites in Cuba.[14),15] The increased corrosion rate along with exposure was also observed for sheltered copper at the marine site in Cuba, and for unsheltered copper at some sites in Ibero-America.[13),14]

Relative humidity, airborne salinity, and SO₂ concentration were reported as the important factors effecting corrosion of copper.[1),4),14),16)-19] The direct effect of rain was excluded for sheltered copper. The corrosion rates at Vung Tau were much higher than those at My Tho and Bien Hoa, clearly due to the higher airborne salinity at Vung Tau. Salinity can be assigned to the main reason leading to the difference in corrosion rate at My Tho and Bien Hoa. The airborne salinity and SO₂ concentration at HoChiMinh were highest compared to those at the other sites. However, the corrosion rate was comparable with that at My Tho and much lower than at Vung Tau. In short, the corrosion rate behaviour of sheltered copper could not be explained by using average SO₂ concentration, airborne salinity, and humidity. Perhaps, the loose corrosion layer at Vung Tau might be a reason of the high corrosion rate there. The loose corrosion layer is assigned to the attack of chloride ions in dry season when very high airborne salinity was observed. The b value about 1.2 at Vung Tau indicates that corrosion layer in marine environment stimulates corrosion of copper, i.e. the loose corrosion layer formed at marine site was a good medium for absorption of moisture and corrosive species including oxidants.

The high corrosion rates of the 3-month sheltered specimens at My Tho, Vung Tau, and Bien Hoa in dry season related to the high airborne salinities in dry season. At HoChiMinh, the lowest airborne salinity was seen in the period from October to December (Q4), while those of the other period were 1.5 times higher. However, the corrosion rate was the highest in the period from April to June (Q2), and almost unchanged in the other 3-month periods in a year. Thus, the effect of chloride was clearly pronounced in the environments with low SO₂ level, but hindered in the environments with high SO₂ level like HoChiMinh.

4.1.2 Unsheltered specimens

The corrosion rates around 2 µm/year at HoChiMinh and My Tho were comparable with those for industrial site, but higher than those for urban and rural sites already reported in literature.[11),13)-15] At Vung Tau it was about 5 µm/year, much higher than the observed value reported for marine site.[1),13)-15]

It was clearly shown on the XRD patterns obtained that Cu₂O is the main and predominating corrosion product of copper. It should be emphasized that the intensity of Cu₂O on the skyward side of unsheltered specimens was always higher than on the groundward ones. Considering that the skyward side was washed by rain more than the groundward side, the growth of cuprite was certainly faster on the skyward side than on the groundward side in any environment, which implies the higher corrosion rate on the skyward side.

As in the case of sheltered copper, the corrosion rates of unsheltered copper were not in accordance with SO₂ concentration in the air at the sites. Also, we cannot find any relation between corrosion rate, and rainfall and number of rainy days. The corrosion rates appeared to associate with the airborne salinities at the sites. The extremely high corrosion rate at Vung Tau corresponded to the extremely high airborne salinity. The approximately equal corrosion rates at other sites were a consequence of the slightly different airborne salinities there. The slightly lower corrosion rate at HoChiMinh among those sites was assigned to the low relative humidity at HoChiMinh, and the slightly higher corrosion rates at Bien Hoa and My Tho compared to those at HoChiMinh were assumed to the higher relative humidity at Bien Hoa and My Tho.

Concerning a short-term corrosion rate of the 3-month specimens, it was clearly seen that the high short-term corrosion rates observed in dry periods at Vung Tau and My Tho were a consequence of the high airborne salinities. Although the airborne salinity at Vung Tau of the period from July to September was lower than that of the period from October to December, the corrosion rates of the two periods were comparable. It was considered as a consequence of the higher relative humidity of the first period. The short-term corrosion rate at My Tho was very high in the period from October to December although the airborne salinity, relative humidity, and rainfall in this period

were similar or lower than those of the period from July to September. We believe that like in the case of sheltered specimens the high monthly airborne salinity in December at My Tho and consequently the loose corrosion layer was a reason of the high corrosion rate. The short-term corrosion rate at HoChiMinh was stable, perhaps owing to the small unchanged airborne salinity around year. However, we could not explain the variation in corrosion rate at Bien Hoa.

As it was mentioned before, the corrosion layers formed in the absolute dry periods at My Tho and Vung Tau were poor-adherent. The big seasonal variation in corrosion rate and physical properties of corrosion layers at My Tho and Vung Tau implies that a long-term corrosion rate may depend on a season when an exposure begins. Hence, a further study of a seasonal effect on long-term corrosion rate would be very interesting.

We can not find a relationship between corrosion rates, rainfall, pH and composition of rain, not for short-term nor for long-term exposure. This implies that rainfall should have minor effect on copper corrosion in comparison with airborne salinity.

4.1.3 Comparison of sheltered and unsheltered specimens

The corrosion rate of copper under shelter was always lower than that without shelter for any exposure period in any environment. This was reasonable since the unsheltered specimens were exposed to more windy places and were under direct attack of rain, and sunlight. The ratios between the corrosion rates of unsheltered and sheltered copper (TL_{un}/TL_{sh}) evaluated for the 1-year exposure were around 2, 3, 5, 6 at HoChiMinh, My Tho, Vung Tau and Bien Hoa, respectively. With time those ratios decreased remarkable at My Tho and Vung Tau, especially at Vung Tau, but slightly changed at HoChiMinh and Bien Hoa. This can be seen from the difference in the b value under sheltered and sheltered conditions given in Fig. 3. The decrease of the ratios TL_{un}/TL_{sh} is a consequence of an accumulation of pollutants in corrosion layers under sheltered condition and wash-off of pollutants from corrosion layer by rain under unsheltered condition. Considering that the environments at HoChiMinh and Bien Hoa are sulphur-dominating, while those at Vung Tau and My Tho are chloride-dominating, again it some conclusion can be stated that the most important pollutant influencing on TL_{un}/TL_{sh} should be chloride.

4.1.4 Realation between corrosion rate and color of copper patina

It is very important to note that the high corrosion rates were observed for the red-purple coloured specimens, while the low corrosion rates were found for the specimens with brown colouring despite exposure methods. As re-

ported in literature, the brown and purple patinas have different morphologies.[20] Consequently, there was a relation between corrosion rate and morphology of copper patina. Some author also suggested the same idea for the corrosion of copper in the initial state of corrosion.[3,11]

From the discussions above, chloride deposition was the most important factor effecting corrosion of copper in Vietnam, and then relative humidity. Sulphur dioxide also effects on corrosion rate but moderately. Also, the corrosion rates of copper in south of Vietnam were higher than those reported in literature for the sites with the similar pollution and chloride deposition levels but located in moderate climatic regions. We consider that the reason might be the high temperature in tropic which weakened the protection barrier of the corrosion layer by enhancing the deep penetration of chloride ions into corrosion layer, thereby increased the corrosion rates.

4.2 Implication of the mass gains and mass losses

The mass gain/mass loss ratio associates with the nature of corrosion products. Cuprite (Cu_2O) is the first corrosion product of copper and has the lowest mass gain/mass loss ratio (0.13) among corrosion products of copper. For $CuSO_4$ this ratio is 1.5. It also depends on a wash-off level as well as a level of substances that can be deposited on corrosion layer through wet and dry depositions.

4.2.1 Sheltered specimens

Corrosion products are considered to remain on sheltered specimens. The mass gain/mass loss ratios for the sheltered specimens at all sites were higher than the theoretical one of Cu_2O. The mass gain/mass loss ratios increased with the increase of SO_2 concentrations in the air (Table 2, Fig. 5). This fact suggests that a higher SO_2 concentration in the air resulted in a higher portion of sulphate products in corrosion layer, consequently on a higher mass gain/mass loss ratio.

4.2.2 Unsheltered specimens

The mass gain/ mass loss ratio less than 0.13 of the unsheltered specimens exposed in rainy periods implies that rains washed off a part of corrosion products. Hence, it was not surprising that the mass gain/mass loss ratios of the 3-month specimens at a particular site were reverse proportional to the rainfalls over exposure periods. The mass gain/mass loss ratio seems also to decrease with the increase of SO_2 concentration as in the case of HoChiMinh and Bien Hoa, where the rainfall at Bien Hoa was higher than that at HoChiMinh but mass gain/mass loss at HoChiMinh was lower compared to that at Bien Hoa. Taking into account all the above, one reason of low mass gain/mass loss ratio at HoChiMinh is a formation of more soluble sulphate product due to the higher concentration
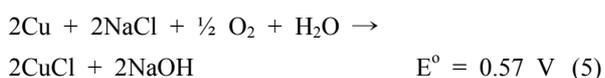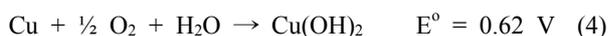
of SO_2 in the air. The extremely low mass gain/mass loss observed for the 3-month specimens of the dry periods at Vung Tau was a consequence of the exfoliation and fall of corrosion products even without the attack of rains as mentioned before. Overall, very low mass gain/mass loss (even minus value) observed at Vung Tau after long exposure was a consequence of the exfoliation and fall of corrosion products, and perhaps the wash off of soluble cuprous complex formed at the high chloride deposition as described in the next section.[22)-23)]

Considering the big variation in the mass gain /mass loss ratios of copper, the mass gains were unable to reflect correctly corrosion rates of copper neither under sheltered nor under unsheltered conditions.

4.3 Evaluation of formation and development of corrosion products

4.3.1 Cuprite

According to the standard electrode potential, the reduction of hydrogen ions cannot be a cathode reaction of copper corrosion. Under normal atmospheric conditions, the most possible cathode reaction of copper corrosion is the reduction of oxygen owing to the abundance of oxygen in the air. The standard potentials of copper oxidation with oxygen depolarization are as follows

$$2Cu + \tfrac{1}{2}\,O_2 \rightarrow Cu_2O \qquad E^o = 0.76 \ V \quad (3)$$

$$Cu + \tfrac{1}{2}\,O_2 + H_2O \rightarrow Cu(OH)_2 \qquad E^o = 0.62 \ V \quad (4)$$

$$2Cu + 2NaCl + \tfrac{1}{2}\,O_2 + H_2O \rightarrow$$
$$2CuCl + 2NaOH \qquad E^o = 0.57 \ V \quad (5)$$

From the viewpoint of thermodynamics, in the abundance of oxygen the oxidation shifts toward the formation of cuprite (3). This is in agreement with the observed that cuprite is the preliminary corrosion product of copper. The other substances of copper are considered as products of the subsequent reactions of cuprite. However it was not excluded that the reaction (5) could take place in the chloride-rich environment.
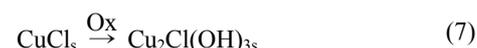
4.3.2 Brochantite and posnjakite

The green stains on the specimens at HoChiMinh, My Tho, and Bien Hoa were assigned to brochantite and posnjakite, since these products were frequently detected there. Moreover posnjakite was formed earlier than brochantite. The green stains developed on the top of the cuprite layer that formed previously. Some authors also reported a similar formation of sulphur-containing products. I. W. Odnevall, J. D. Nairin and other researchers showed SEM image of natural copper patina where crystals of sul-

phur-containing products of copper were seen over the top of cuprite layer.[6),24)] The above was in the agreement with the depth profile of sulphur and chlorine obtained by M. Watanabe who found that sulphur distributed near the surface of corrosion layer, while chloride distributed in depth, and the different in-depth distribution of sulphate and chloride related with the different ionic radii of those ions.[25)]

Effect of chloride - A delayed formation of brochantite was found to accompany the formation of atacamite or fast development of nantokite. The formation of atacamite or nantokite is a consequence of a high deposition of chloride. Thus, high amounts of chloride delay the formation of brochantite.

4.3.3 Nantokite and atacamite

Normally nantokite was the first chloride corrosion product of copper followed by atacamite. However, the formation of atacamite could bypass the formation of nantokite at very high chloride deposition as in the case of the specimens at Vung Tau. The formation of nantokite and atacamite can be described by the following equations

$$\text{Increasing of Cl}^- \downarrow \quad \begin{cases} Cu_2O_s \rightarrow CuCl_s & (6) \\[2mm] CuCl_s \xrightarrow{Ox} Cu_2Cl(OH)_{3s} & (7) \end{cases}$$

$$Cu_2O_s \xrightarrow{Ox} Cu_2Cl(OH)_{3s} \qquad (8)$$

From the above standpoint, at a chloride-rich environment such as Vung Tau the reaction (8) should take place, while in a medium-chloride environment such as HoChiMinh, My Tho and Bien Hoa nantokite would form first by the reaction (6). The reaction (7) and (8) takes place when chloride accumulates in corrosion layers at high level. Therefore, nantokite increases during exposure and decreases afterward with formation of atacamite as in the case of the unsheltered specimens at HoChiMinh and My Tho.

From obtained results the formation of atacamite and nantokite was more potential in dry period when the supply of oxidant and chloride is more sufficient owing to the lack of rain and consequential scarcity of water on the surface. Also, nantokite was less frequent on the skyward side of the unsheltered specimens than on the groundward side. Perhaps chloride on the groundward side was more than on the skyward side due to washing by rains. The formation of atacamite on highly chloride-contaminated copper surface can be explained by the formation of chloride complex which resulted in the higher pH thus promote the precipitation of basic copper chloride as follows.

$$Cu_2O_s + 4Cl^- + H_2O \rightarrow 2[CuCl_2]^- + 2OH^- \qquad (9)$$

$$CuCl_s + Cl^- \rightarrow [CuCl_2]^- \qquad (10)$$
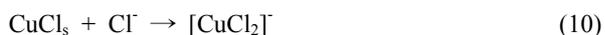
The formation of copper (I) complex was regarded as a reason of the high porosity of the purple patina formed in a chloride-rich environment,[22)-23)] which resulted in the high corrosion rate. According to the result obtained by M. Watanabe, chloride ions diffuse deeply into cuprite layer. Moreover, high temperature and week protective layer accelerate deeper penetration of chloride ions. Those conditions just existed at Vung Tau. Consequently, atacamite would form in deep as seen at Vung Tau. There, the green layer of atacamite formed under the top layer of cuprite and caused the exfoliation of the cuprite layer.

4.3.4 Other corrosion products

The fact that langite and cupric hydroxide were not found at HoChiMinh implies that they form only in low SO_2-environments. In addition, cupric hydroxide was detected only on the sheltered specimens or groundward side of the unsheltered specimens means that cupric hydroxide is easily washed off by rain. Botallackite - the isomorphous form of atacamite was found at Vung Tau only, i.e. its formation required very high chloride deposition.

5. Conclusion

1) Corrosion rate of copper under sheltered conditions was lower than under unsheltered conditions.

2) In South Vietnam the most important factor effecting corrosion of copper under sheltered and unsheltered conditions is a chloride deposition, followed by a relative humidity. The effect of SO_2 on copper corrosion was moderately. The seasonal variation in corrosion rate of copper is a consequence of the seasonal variation in chloride deposition. The fasted corrosion rate of copper was observed in marine-urban environment both under unsheltered and sheltered conditions. In addition, there the corrosion rate of copper under sheltered condition increased along with exposure.

3) The mass gain/mass loss ratio for sheltered copper increased with SO_2 concentration in the air. Under unsheltered conditions, rain washed off a part of corrosion products. The wash-off level was proportional to the rainfall over exposure period and it was very high in the marine site. SO_2 concentration in the air might increase wash-off level of the corrosion products. Mass gain can not be used as a measure of the corrosion rate neither under sheltered conditions, nor under unsheltered conditions.

4) The copper patina formed in sulphur-rich environment was coloured to brown and then to greenish-grey, while in chloride-rich environment it was purple or red-purple. The red-purple patina was porous and poor-adherent to the substrate. High corrosion rate corresponded to the red-purple patina.

5) The preliminary and dominating corrosion product of copper was cuprite that increased during an exposure in spite of environmental condition and exposure method. Brochantite and posnjakite were the common corrosion products found at all sites. Nantokite was corrosion product of copper in moderate-chloride environment, while atacamite was the product in chloride-rich environment. Posnjakite and nantokite seemed to transform into brochantite and atacamite at prolonged exposure, respectively. Chloride ions hinder a growth of brochantite.

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