

## Atmospheric Corrosion of Copper in Urban, Rural/Coastal, and Hot Spring Areas in Japan

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### INTRODUCTION

Copper corrosion in the atmosphere has been studied extensively since copper is a typical material used in electronics [1-3]. Copper corrosion products formed during field exposure have been analyzed using several analytical techniques. Nassau *et al.* [4] have shown that copper patinas formed during outdoor exposure are composed of cuprite  $\text{Cu}_2\text{O}$ , brochantite  $\text{Cu}_4\text{SO}_4(\text{OH})_6$ , antlerite  $\text{Cu}_3\text{SO}_4(\text{OH})_4$ , posnjakite  $\text{Cu}_4\text{SO}_4(\text{OH})_6 \cdot \text{H}_2\text{O}$ , and atacamite  $\text{Cu}_2\text{Cl}(\text{OH})_3$ . Although copper patinas formed during long exposure periods such as a year or more have been studied, little attention has been paid to the analysis of copper patinas formed during short exposure periods such as a month, and this is important in terms of understanding the initial stages of copper corrosion. In this study, we analyzed the corrosion products that formed on copper plates exposed in urban, rural/coastal, and hot spring areas in Japan during one summer month [5].

### EXPERIMENTAL

The copper plates used in this study were 99.9% pure, and 42 x 25 x 0.2 mm in size. Their surfaces were cleaned with acetone and nitric acid, and they were then dried in nitrogen prior to exposure.

The copper plates were exposed outdoors at our telephone switching centers located in urban, rural/coastal, and hot spring areas. We selected Tokyo, Ibaraki, and Tochigi as the urban, rural/coastal, and hot spring areas, respectively. The copper plates were exposed for a month in summer.

After the exposure, we analyzed the corrosion products on the copper plate using several analytical techniques including X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD).

### RESULTS AND DISCUSSION

#### *Qualitative analysis of corrosion products by XPS*

The S 2p XPS spectra showed that sulfate was the predominant state on the copper surfaces exposed in Tokyo (urban) and Ibaraki (rural/coastal). This indicates that copper sulfates exist in the corrosion products. For the copper exposed in Tochigi (hot spring), the S 2p XPS spectra revealed the coexistence of sulfate and sulfide. Sulfide could be the predominant sulfur state in Tochigi because the product of the reaction between copper and hydrogen sulfide is copper sulfide. However, the XPS results showed that sulfate was predominant. This could have been due to the oxidation of sulfide to sulfate at the copper surface during exposure. Therefore, the origin of the sulfate was different from that found in Tokyo and Ibaraki.

#### *Phase identification by XRD*

The XRD patterns of copper exposed in Tokyo and Ibaraki revealed that cuprite and posnjakite formed. Nassau *et al.* detected posnjakite in copper patinas exposed for a year [4] and its intensity weakened with exposure time. Odnevall *et al.* [6] reported the existence of posnjakite in corrosion products exposed in a rural

area, but they could not detect posnjakite on copper exposed for a short time. Our results clearly showed that there was posnjakite in the corrosion products of copper exposed for a month, so we believe that posnjakite is formed initially when copper is exposed in urban and rural/coastal areas. By contrast, the XRD pattern of copper exposed in Tochigi showed only cuprite peaks although the amount of sulfur in the corrosion products was the highest. This could have been due to the different sulfate origins as discussed above.

We could not detect any chlorine-containing phases such as atacamite even on the copper surfaces exposed in Ibaraki. This result indicates that the atacamite formation rate might be slow and/or the chlorine-containing phases were not crystallized.

### CONCLUSION

XRD patterns showed that posnjakite and cuprite were formed on copper surfaces exposed in urban and rural/coastal areas. By contrast, cuprite was the only corrosion product that formed on copper exposed in a hot spring area. This could have been due to the differences in the origin of sulfate. Posnjakite is initially formed as copper sulfate when copper plates are exposed in urban and rural/coastal atmospheres.

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