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Effects of Gaseous Pollution and Thermal Conditions on the Corrosion Rates of Copper and Silver in Data Centre Environment: A Literature Review

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ABSTRACT

The objectives of the present review are to: 1) summarize the existing knowledge on the mechanisms of the corrosion, identify and analyze the major factors affecting the corrosion of copper and silver; 2) compare various measurement techniques for the study of atmospheric corrosion and models of corrosion; 3) identify knowledge gaps for atmospheric corrosion; 4) recommend “realistic worst case” pollution levels for laboratory testing of humidity and temperature effects on corrosion and assessment of datacom equipment reliability in data centers. This review focuses on the five pollutants: SO₂, NO₂, H₂S, O₃ and Cl₂. Results of the review include: the pollution levels and thermal environmental conditions in data centers; fundamental mechanisms of corrosion; current knowledge of the major factors affecting the corrosion rates of copper and silver; the techniques (QCM, Coulometric Reduction, SEM, XPS, FTIR and EIS) for the measurement of corrosion levels. It was found that the “realistic worst-case” concentrations for H₂S, NO₂, SO₂, Cl₂ and O₃ are 10 ppb, 80 ppb, 40 ppb, 2 ppb and 60 ppb, respectively. Different levels and combinations of contaminants, temperature, relative humidity and air velocity cause different corrosion on the metal. Chloride, Nitrogen dioxide and Sulfur dioxide are the common corrosive gases for the datacom equipment. Hydrogen sulfides and ozone are very important gaseous contamination in data center environment. Each of them alone can damage the equipment, and their synergistic effects with the other compounds and humidity can cause significantly more damages, but a mechanistic model is lacking for predicting the synergistic effects and better design of the thermal environment to ensure equipment reliability while improve the energy efficiency through the use of outdoor air for free cooling.

KEYWORDS

Atmospheric corrosion, copper, silver, SO₂, NO₂, H₂S, O₃ and Cl₂

INTRODUCTION

Data centers have the highest energy usage intensity among all building types and consume increasingly more energy due to the significant increase in the number of data centers worldwide. In an effort to reduce energy consumption, an increasing number of data centers have adopted air-side economizers to enable “free-cooling”. However, gaseous and particulate contaminants can enter data center when using air-side economizers, which may cause environment-related IT and Datacom equipment failures. Due to lack of data on the severity of the corrosion effects under realistic concentration levels and thermal environmental condition, gaseous contamination limits for the reliable operation of electronic equipment cannot be specified presently in terms of the concentration of gaseous contaminants in the air. ITEs can operate in a wide range of thermal environmental conditions including relative humidity levels up to 80% according to the current standards (ASHRAE, 2012c). There is clearly a need to determine the allowable gaseous concentration limits for the data center environment, especially under higher relative humidity conditions.

The objectives of the present review are to summarize the existing knowledge about the mechanisms of the corrosion, compare various measurement techniques for the study of atmospheric corrosion, identify knowledge gaps for atmospheric corrosion and recommend the “realistic worst case” pollutant levels and thermal environmental conditions for corrosion testing and assessment for data center applications.

MECHANISM OF ATMOSPHERIC CORROSION

Atmospheric corrosion is one kind of electrochemical corrosion. It occurs at the metal-solution interface with the creation of cathodic and anodic sides of the metal surface. The anode and cathode reactions in atmospheric corrosion are shown in Equation (1) and (2):

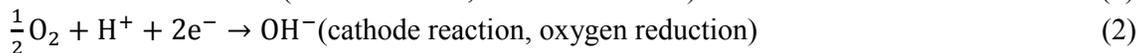
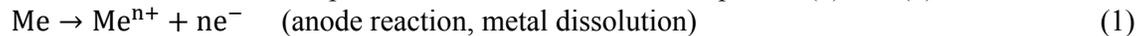


Figure 1 shows various processes involved in the atmospheric corrosion of copper based on the existing finding from the literature (T. Aastrup, 2000).

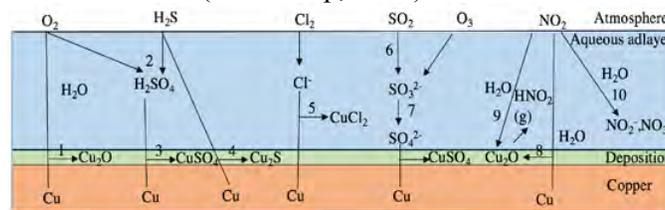


Figure 1 A schematic description of the atmospheric corrosion of copper

In the case of corrosion of ITEs, because the air is strictly controlled to have a dew point lower than the surface temperature of ITEs components to avoid apparent condensation, the aqueous layer above is likely to be only a thin layer or multi-layer of H₂O molecules adsorbed on the surface. Without the presence of contaminants, O₂ can diffuse into the aqueous layer and react with the pure copper to form a layer of copper oxide, a deposition layer that would protect the copper from corrosion. However, the gaseous pollutants, if present, can be dissolved into the adsorbed water molecules and react with O₂ to form H₂SO₄, which then reacts with copper to form copper sulfates. H₂S can also react directly with copper and O₂ to form copper sulfides (Processes 1 through 4 above).

When chlorine dissolves in the aqueous adsorption layer (adlayer), it resolves to the chloride ions. And these ions can react with the copper, which causes the copper dissolves into the liquid regime. Sulfur dioxide react with ozone in the liquid regime and ozone oxidizes the sulfur dioxide to H₂SO₄. Then H₂SO₄ combines with copper to generate the CuSO₄. NO₂ dissolves in the liquid regime and create HNO₂. And it has a reaction between HNO₂ and Cu to get the products of Cu₂O and HNO₂(gas). NO₂ also generates NO₂⁻ and NO₃⁻ after dissolving in the liquid. (Processes 5 to 10 above). While the reaction processes can be identified qualitatively, data are lacking on the reaction rate constants for the various processes identified above, and the synergistic effects of the various compounds under different relative humidity and temperature conditions cannot be readily determined from the existing literature.

FACTORS AFFECTING THE CORROSION RATES OF COPPER AND SILVER

Relative humidity

Primary, secondary and tertiary values of Critical Relative Humidity have been defined as the values of relative humidity below which no corrosion of the metal in question takes place, at which corrosion occurs rapidly, and above which further acceleration of corrosion can be

observed (if exists). The primary value of critical RH for uncorroded metals seems to be virtually independent of type of metals, which depends on the type of pollutants and moisture content (and hence the temperature for the given relative humidity level) in the atmosphere (Vernon, 1935). But the secondary and tertiary (if exists) values vary quite widely, depending on the presence and levels of gaseous pollutants and their potential synergistic effects as well as the metal type (Syed, 2006).

Air temperature

For a given moisture content (or specific humidity) in the moist air mixture, an increase in temperature reduces the level of relative humidity, resulting less water molecules being adsorbed on the material surface, and hence leads to a less amount of soluble pollutant's deposition on the surface and would likely reduce the corrosion effect (Mohan, 1991). However, on the other hand, a higher temperature tends to increase the reactivity of the ionization processes involved in the corrosion, and hence could enhance the corrosion effect (Franey, 1985). Therefore, the tradeoff between these two opposite effects needs to be evaluated for specific pollutant or pollutant mixture.

Sulfur dioxide

Sulfur dioxide is the most common corrosive gas for the Datacom equipment. Combustion of all fossil fuels can form the sulfur dioxide. Copper exposed to 80% RH, and 200 ppb SO₂ for approximately 1000 minutes formed copper sulfite, probably as a CuSO₃-xH₂O-like species, and cuprous (Cu₂O-like) oxide as major corrosion products (T. Aastrup, 2000). Similar results were also obtained by Erikson (1993).

Nitrogen Dioxide

Nitrogen dioxide source is the high-temperature combustion and biomass burning. Natural phenomenon like lightening also forms NO₂. According to Eriksson (1993), NO₂ has very small corrosive effects alone even in the ppm range. Muller (1991) also found that nitrogen dioxide had little influence on the corrosion rate of silver. The data reviewed above indicates that the NO₂ alone is not a significant factor for corrosion, but it can accelerate corrosion through synergistic effect with SO₂. Data on its possible synergistic effect with other gases of interests such as O₃, H₂S, and Cl₂ under different humidity and temperature conditions are lacking.

Hydrogen sulfide

Hydrogen sulfides is the most important gaseous contamination in the data center. It can cause the serious corrosion on the circuit board. Hydrogen sulfide is formed by the fossil fuel processing and combustion and natural processes (decay of vegetation in soils and wetlands, excess sulfur emission from vegetation and the like). There are two common modes of hardware which will be damaged if they are exposed to the sulfur-bearing gases (H₂S, SO₂): printed circuit boards (PCBs) and miniature surface-mount technology (SMT) resistors. Trana (2003) found that after the copper was exposed in this condition, copper sulfide was formed. Exposure to a higher concentration of H₂S resulted in a faster and larger increase of the thickness of Cu₂S, as expected. The data also show that there appears to be a maximum thickness of Cu₂S of 8-10 μm, beyond which further increase of exposure time had little impact on the thickness. It is possible that at this thickness, the Cu₂S layer became a significant resistance to the diffusion of ions between the adsorbed moisture layer and the pure copper, and hence slowed down the electrochemical process that was responsible for the corrosion. It is noted that even at 10 ppb (the proposed realistic worst-case level), 0.1 μm of corrosion layer was measured after 3 days of exposure (T.T.M.Trana, 2003).

Ozone

Natural and anthropogenic electrical discharge is the source of the ozone. It can increase the corrosive effect for the copper and silver (T. Aastrup, 2000). Ozone also enhanced the copper sulphadation when copper was exposed in SO₂ with ozone (T. E. Graedel, 11 May 1984).

Chloride

Chloride has limited corrosive ability to copper or silver. But it has a large influence on these metals when it combines with the hydrogen sulfide. In the study by Muller (1991), the copper and silver were exposed to 1.9 ppb of Cl_2 at 22°C and $50 \pm 5\%$ RH for one month. The results show that chloride alone had mild corrosion effect, similar to that of SO_2 tested, but significantly weaker than that of H_2S . Data are lacking on the synergistic effects of Cl_2 with other gasses, and for different RH and temperature conditions. When copper is exposed in H_2S , Cl_2 and NO_2 , the role of Cl_2 is to remove the Cu_2O then other pollutants can attack Cu directly (Abbott, 1988).

Synergistic effect

Figure 2 shows the corrosion thickness as a function of pollutant exposure amount (concentration times duration) found by previous researchers. The combined effects of different pollutants and relative humidity are very complex, and not yet well understood. Data is especially lacking under field concentration levels which are typically much lower than those used in the laboratory studies.

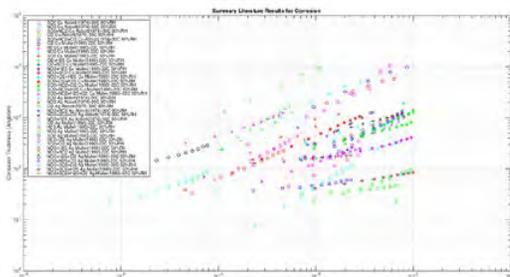


Figure 2 Summary Literature Corrosion Results

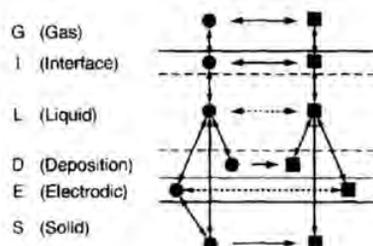
Chloride, Nitrogen dioxide and Sulfur dioxide are the common corrosive gases for the Datacom equipment. Each of them alone can cause only a small amount of corrosion on the metallic surfaces, even though some corrosion products can be detected on the surfaces of the materials. However, their co-existence can cause significant corrosion to ITEs due to synergistic effects among them Muller (1991). Cl_2 , H_2S , NO_2 and SO_2 can all cause significant damages to silver

surface. But for coppers, H_2S and Cl_2 can cause the most damage. Hydrogen sulfides and ozone are very important gaseous contamination in data center environment. Each of them alone can damage the equipment, and their synergistic effects with the other compounds can cause even more damages (T. Aastrup, 2000). The catalytic mechanism can increase the reaction speed but cannot produce additional products. It is necessary to consider the synergistic effect to assess the risk of ITE failure in a polluted environment. Such studies are lacking and need to be pursued in order to develop a reliable method for failure predictions.

MODELING OF ATMOSPHERIC CORROSION

In the data center, gaseous contaminations can include SO_2 , H_2S , NO_2 , Cl_2 , and H_2S . They can corrode the metallic materials and damage the circuit boards, connectors and various other electronic components. From the multi-regime perspective on atmospheric corrosion chemistry (Graedel, 1996), six regimes can be identified (Figure 3-1): G (gas), I (interface), L (liquid), D (deposition layer), E (electrode regime) and S (solid). Study of different layers requires knowledge of different science fields: gas layer – atmospheric chemistry; interface layer – convective and diffusive mass transfer and interface thermodynamics; liquid layer – freshwater, marine, and brine chemistry; deposition layer – colloid chemistry, surface science, and mineralogy; electrodic layer – electrochemistry; and solid layer – solid-state chemistry.

In this model, for the gas regime, pollutant gases by convection or detrainment from interface get into this regime. Then some of the gases deposit on the interface. Some species have chemical interaction with each other. When they arrive at the interface, some of them will volatilize into the gas regime and some enter into the liquid regime. In the interface regime, there are some chemical transformations among different



species. In the liquid regime, the species not only can reach the deposition regime but also can directly reach the electrodic regime and the solid regime. Chemical transformation can take

place at each regime. For the species in the solid regime, they react with species which come from the liquid regime and electrodic regime. The electrodic regime is where electrochemical reaction takes place. Copper loses its electrons and becomes the copper ions which get into the electrodic regime. Oxygen which is in the liquid regime reacts with the copper ions to generate the depositions. The circle and square symbols represent different species. When the corrosion products are generated over the surface, they will become more resistant to the corrosion process. The research of T.T.M.Tran (2003) shows that Cu_2S is an important resistance of diffusion of the ions between the liquid regime and the solid regime.

MEASUREMENT TECHNIQUES

In order to analyze the corrosion, there are many techniques for monitoring the mass change and for analyzing the geography of surface and surface compositions. Quartz crystal microbalance (QCM) is a technique to detect the mass change of the materials using the piezoelectric effect. In scanning electron microscopy (SEM), the information of topography and composition on the surface can be gained. X-ray photoelectron spectroscopy (XPS) is for the solid surface. It can be applied for the oxide thickness measurements. It can identify all elements except for hydrogen. In Fourier transform infrared spectroscopy (FTIR), it is useful for identifying the “chemical family” of a substance. An electrochemical impedance spectroscopy (EIS) is very useful for detecting the atmospheric corrosion. It measures the corrosion rate by estimating the polarization resistance, which is based on the theory of AC impedance. This technique is useful on high resistance materials and non-destructive. Coulometric Reduction is an electrochemical-based technique. This technique measures the thickness of the film by monitoring the quantity of electricity which is forming during the chemical reaction between the electrolyte and the corrosion products.

RECOMMADATION FOR THE “REALISTIC WORST-CASE CONCENTRATION LEVELS”

Table 1. Summary of Pollutant Concentrations and Recommended Limits by IEC (2002), Telcordia (2006), ISA(1985) and One Manufacturer’s Internal Standards

Gas	H_2S		SO_2		Cl_2		NO_2		O_3	
	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min
Measurement (ppb)	8310008	0.101	87	0	0.58	0	152	0	174	0
Limits (ppb)	40	2	50	10	35	1	700	50	123	2

Table 1 shows the measurement data of outdoor pollutant levels and the concentration limits recommended for IT equipment protection against corrosion. The current guideline gives the recommended temperature and relative humidity envelope: the dew point is from $-9\text{ }^\circ\text{C}$ to $15\text{ }^\circ\text{C}$; The dry-bulb temperature is from $18\text{ }^\circ\text{C}$ to $27\text{ }^\circ\text{C}$ and the relative humidity is less than 60%. We propose the following as the “realistic worst- case concentration levels” for the MFG testing (Table 2)

Table 2. Proposed “Realistic Worst Case” Concentrations for Mixed Flow Gas (MFG) Testing

Pollutant	H_2S	NO_2	SO_2	Cl_2	O_3
Concentration (ppb)	10	80	40	2	60

The values in the table are consistent with the guideline limits for G2 (moderate) levels of corrosion per the ANSI/ISA Standard 71.04-2013.

SUMMARY AND CONCLUSIONS

It was found that the “realistic worst-case” concentrations for H₂S, NO₂, SO₂, Cl₂ and O₃ are 10 ppb, 80 ppb, 40 ppb, 2 ppb and 60 ppb, respectively. Chloride, Nitrogen dioxide and Sulfur dioxide are the common corrosive gases for the datacom equipment. Hydrogen sulfides and ozone are very important gaseous contamination in data center environment. But the lack of knowledge is about the synergistic effect at different thermal environmental conditions. There is lacking for a mechanistic model to predict the synergistic effects combining with various thermal environment.

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