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Abstract

The effects of moisture content, temperature, and pollutant mixture on atmospheric corrosion of copper and silver were investigated by exposing test specimens to different environmental conditions, followed by surface characterization using the coulometric reduction, Scanning Electron Microscopy and Energy Dispersive Spectrometry (SEM/EDS). Printed circuit board test cards (PCBs) with bare copper were also used to investigate the effects of voltage bias on the PCBs on the corrosion rate. The test specimens were exposed to mixed flowing gases (MFG) environment with eight different combinations of the following five pollutants at the fixed concentration levels: 60 ppb O₃, 80 ppb NO₂, 40 ppb SO₂, 2 ppb Cl₂, and 10 ppb H₂S. Temperature and relative humidity (RH) were varied from a reference condition (21°C and 50% RH which is within the current ASHRAE-recommended thermal envelope) to a higher value (28°C, 70% RH or 80% RH) to increase the moisture content of the test environment. Test results revealed the dominating effect of Cl₂ on the copper corrosion and that of H₂S on the silver corrosion. Increasing the moisture content at 21°C caused more severe corrosion of copper when Cl₂ was present, but not for silver. When temperature was increased from 21°C to 28°C at 50% RH, it reduced the corrosion of copper, but not for silver. Voltage biased PCBs had a less effect on corrosion than PCBs without the voltage bias. A mechanistic model based on the multi-ion transport and chemical reactions was also proposed to predict the corrosion of copper due to Cl₂-containing pollutant mixtures. The model's prediction of the effects of temperature and RH agreed well with the experimental results. These findings provided the basis for possible expansion of the ASHRAErecommended thermal envelope for data centers when Cl₂ and H₂S are not present and limiting the

thermal envelope when Cl_2 or H_2S is present. They also improved the understanding of the corrosion mechanisms for the copper when Cl_2 is present in the data center environment.

EFFECTS OF AIR POLLUTION, TEMPERATURE AND MOISTURE CONTENT ON COPPER AND SILVER CORROSIONS AND THE RELIABILITY OF DATA CENTER EQUIPMENT

by

Rui Zhang

B.S., Shenyang Jianzhu University, 2014 M.S., Syracuse University, 2016

Dissertation Submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Mechanical and Aerospace Engineering

> Syracuse University May 2021

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Abstract	i
Acknowledgements	V
Table of Contents	vii
List of Figures	X
List of Tables	.XV
1. Introduction	1
1.1. Background	2
1.2. Objectives and Scope	3
1.3. Organization of this Dissertation	4
2. Literature Review	6
2.1. Gaseous Pollutant Levels and Thermal Conditions in Data Center Environment	6
2.1.1. Pollutant Levels	6
2.1.2. Thermal Environment	.23
2.2. Fundamentals of Atmospheric Corrosion	.25
2.3. Factors Affecting the Corrosion Rates of Copper and Silver	.29
2.3.1. Thermal Environmental Conditions	.29
2.3.2. Gaseous Contamination	.35
2.3.3. Synergistic Effect	.42
2.4. Summary	.48
3. Experimental Apparatus and Instrumentation	.51
3.1. Test system composition	.51
3.2. Corrosion Exposure Chamber	.53
3.2.1. Exposure Chamber Design	.53
3.2.2. Material and Airtightness	.54
3.2.3. Uniformity and Flow Rate	.55
3.3. Gas Supply System	.56
3.3.1. Total Supply Capacity and Air Source	.56
3.3.2. Humidity Source	.58
3.3.3. Temperature Control	.59
3.3.4. Corrosive Gas Source	.59
3.3.5. Gas Delivery System	.63
3.3.6. Monitoring System	.64
3.4. Test Specimens	.65
3.4.1. Standard Coupon	.65
3.4.2. Printed Circuit Board (PCB)	.65
4. Experimental Method, Procedure, and Design	.68
4.1. Experimental Method	.68
4.2. Experimental Procedure	.69
4.2.1. Test Chamber Verification	.69
4.2.2. Test Preparation	.71
4.2.3. Test Procedure	.71
4.3. Experimental Design: Test Conditions	.72
4.4. Corrosion Detection and Analysis	.76

Table of Contents

4.4.1. Visual Inspection, Image Analysis, and Color Indexing	76
4.4.2. Coulometric Reduction	78
4.4.3. Scanning Electron Microscopy and Energy Dispersive Spectrometry (SEM/EI	OS).82
4.4.4. Atomic Force Microscopy (AFM)	84
4.4.5. X-ray Photoelectron Spectroscopy (XPS)	86
5. Experimental Results	87
5.1. Corrosion Thickness and Corrosion Products (Coulometric Reduction)	87
5.1.1. Corrosion Development over Time	87
5.1.2. Effects of Pollutant Mixture	90
5.1.3. Effects of Relative Humidity	94
5.1.4. Effects of Temperature	99
5.2. Color Index	103
5.2.1. Corrosion Development over Time	104
5.2.2. Effects of Pollutant Mixture	106
5.2.3. Effects of Temperature	111
5.2.4. Effects of Relative Humidity	115
5.3. Surface Composition (SEM/EDS)	117
5.3.1. Effects of Pollutants Mixture	121
5.3.2. Effects of Temperature	123
5.3.3. Effects of Relative Humidity	124
5.4. Surface Geometry (AFM)	126
5.4.1. Effects of Pollutants Mixture	126
5.4.2. Effects of Temperature	128
5.4.3. Effects of Relative Humidity	130
5.5. Elemental Composition of the Corrosion Layer (XPS)	132
5.6. Effect of Humidity Fluctuation	142
5.7. Effect of Voltage Bias (Electrical Current)	149
5.8. Discussion	153
5.8.1. Corrosion Development over Time	153
5.8.2. Temperature Effect	153
5.8.3. Relative Humidity Effect	154
5.8.4. Individual and Synergistic Effect	156
5.8.5. Effects of Humidity Fluctuation	158
5.8.6. Effects of Voltage Applied to the PCBs	159
5.9. Conclusions	159
6. Corrosion Model Development	163
6.1. Introduction	163
6.1.1. Key Influencing Factors	164
6.1.2. Empirical Models	165
6.1.3. Mechanistic Models	168
6.2. Model Development	185
6.2.1. System and Assumptions	185
6.2.2. Governing Equations	187
6.2.3. Determination of Model Parameters	194
6.2.4. Model Implementation	203

6.2.5. Model Verification	
6.3. Results and Discussion	
6.3.1. Corrosion Thickness Development	
6.3.2. Effects of Relative Humidity	214
6.3.3. Effects of Temperature	
6.3.4. Effects of Multiple Pollutants	217
6.3.5. Limitation of the Model	
6.3.6. Future Work	
6.4. Summary and Conclusions	
7. Conclusions and Recommended Future Studies	
8. Implications for Environmental Control in Data Centers	
8.1. Basis for recommendations	
8.2. Recommendations	
9. Appendix	231
9.1. Appendix 1 - Test Procedure	231
9.2. Appendix 2 – Data of Coulometric Reduction Analysis	
10. Reference	
11. Index	241
12. Vita	

List of Figures

Figure 2-1 2000 – 2015 Pollutant Air O₃, NO₂, and SO₂ Concentration in the U.S. (Retrieved Figure 2-2 Goddard Earth Observing System Version 53GEOS-5/GOCART Monthly Mean of SO₂ Figure 2-3 Outdoor Levels of NO₂ and SO₂ for Selected Cities (World Health Organization, 2000) Figure 2-4 Annual Mean Concentration of SO₂ (μ g/m³) in Europe (EEA) (Retrieved September Figure 2-5 Annual Mean Concentration of O₃ (µg/m³) in Europe (EEA) (Retrieved September 2016 Figure 2-6 Annual Mean Concentration of NO₂ (µg/m³) in Europe (EEA) (Retrieved September Figure 2-7 NO₂, O₃, and SO₂ Concentration in Delhi, India from 2006 to 2016 (Retrieved......14 Figure 2-9 2014 Outdoor Pollutant Levels in Shunyi New Town, Beijing, China (Zhang, 2016)16 Figure 2-10 2014 Outdoor Pollutant Levels in Wan Liu, Beijing, China (Zhang, 2016)16 Figure 2-11 2014 Outdoor Pollutant Levels in Ding Ling, Beijing, China (Zhang, 2016)17 Figure 2-12 2014 Outdoor Pollutant Levels in Changping Town, Beijing, China (Zhang, 2016) 17 Figure 2-13 2014 Outdoor Pollutant Levels in Dong Si, Beijing, China (Zhang, 2016)18 Figure 2-14 2014 Outdoor Pollutant Levels in Temple of Heaven, Beijing, China (Zhang, 2016) Figure 2-16 Thermal Environmental Conditions of Air Entering IT Equipment (A1, A2, A3, and Figure 2-17 A Schematic Representation of the Six Regimes and the Transitions and Transformations (T. E. Graedel, 1996)25 Figure 2-18 A Schematic Description of the Atmospheric Corrosion of Copper27 Figure 2-19 Weight Increase due to Corrosion of Iron Specimens under Different Exposure Figure 2-20 Relative Behavior of Iron, Zinc, and Copper (0.01% SO₂, Increasing Humidity in Early Figure 2-21 Variation of Average Film Thickness with Increasing Temperature for the Silvers (J. Figure 2-24 Variation with Time of the Thickness of Cu₂S during Exposure of Copper at Different Figure 2-27 Copper Coupon Test Data for Cl₂, H₂S, NO₂, and SO₂ (Muller, 1990)44 Figure 2-28 Silver Coupon Test Data for Cl₂, H₂S, NO₂, and SO₂ (Muller, 1990)44 Figure 2-29 Copper Coupon Test Data for Synergistic Effect (Muller, 1990)......45

Figure 3-1 Schematic of the Test System (six of the seven corrosion test chambers were used).	.51
Figure 3-2 Photo of the Test System	.52
Figure 3-3 Schematic Diagram for Exposure Chamber and Sample Holder	.53
Figure 3-4 Actual Exposure Chamber	.54
Figure 3-5 Sample Holder for Coupons	.54
Figure 3-6 3D Printer	.55
Figure 3-7 Air Supply before the Humidifier and Pollutant Generators	.57
Figure 3-8 Air Filter (Left) with Chemi-sorbent (Right)	.57
Figure 3-9 Air Filter System	.58
Figure 3-10 Water Impingers for Controlling Relative Humidity	.59
Figure 3-11 Ozone Generator (Left) and 2B Tech. Model 202 Ozone Monitor (Right)	.60
Figure 3-12 Permeation Tubes for NO ₂ , SO ₂ , H ₂ S, and Cl ₂	.61
Figure 3-13 2B Tech. Models 400/401 NO _x Monitor	.62
Figure 3-14 Actual Mixing Chamber	.63
Figure 3-15 Standard Coupons for Copper and Silver	.65
Figure 3-16 PCB Drawing (Left) and Actual PCB	.67
Figure 4-1 Test Conditions (ASHRAE,2015)	.74
Figure 4-2 Photo Light Box - Side	.76
Figure 4-3 Photo Light Box - Front	.76
Figure 4-4 Correlations Between the Corrosion Thickness and Color Index (RGB difference	e is
equal to RGB of the exposed coupon - RGB of the clean coupon. It represents the change of RG	GB
due to corrosion)	.78
Figure 4-5 a) Secondary and b) Backscattered Electron Micrographs of the Copper Bottom Regi	ion
at high Magnification (15kV), which was exposed under 21°C, 80%RH and MFG+Cl ₂	.83
Figure 4-6 Spectra Locations in Backscattered Electron Micrograph	.83
Figure 4-7 Spectra Profile for Spectrum shown in Figure 4-6	.84
Figure 4-8 Height and Deflection for Copper (Exposed under 21°C, 50%RH and NO ₂ +SO ₂ +	O ₃)
	.85
Figure 4-9 Height and Deflection for Silver (Exposed under 21°C, 50%RH and NO ₂ +SO ₂ +O ₃)	85
Figure 4-10 Cu 2p XPS Spectrum	.86
Figure 5-1 Corrosion Development over Time for Copper and Silver (21 ° C 50%)	RH
$NO_2 + SO_2 + O_3 + H_2S + Cl_2)$.88
Figure 5-2 Corrosion Development over Time - Ratio of Corrosion Products (Cu ₂ O and unkno	wn
products) for Copper	.89
Figure 5-3 Corrosion Development over Time – Ratio of Corrosion Products (AgCl, Ag ₂ S, a	and
unknown products) for Silver	.90
Figure 5-4 Effects of Pollutants Mixture - Copper Corrosion Results after Exposure 6 Da	ays
(Coulometric Reduction)	.91
Figure 5-5 Effects of Pollutants Mixture - Silver Corrosion Results after Exposure 6 Da	ays
(Coulometric Reduction)	.91
Figure 5-6 Corrosion Product Ratio for Different Pollutant Combination - Silver	.93
Figure 5-7 Corrosion Product Ratio for Different Pollutant Combination - Copper	.93
Figure 5-8 Effects of Relative Humidity - Copper Corrosion Results after Exposure 6 Da	ays
(Coulometric Reduction)	.94
Figure 5-9 Effects of Relative Humidity - Silver Corrosion Results after Exposure 6 Da	ays
(Coulometric Reduction)	.95

Figure 5-10 Effect of Pollutant Mixture - Ratio of the Corrosion Product Cu ₂ O – Copper98
Figure 5-11 Effect of Pollutant Mixture - Ratio of the Corrosion Product Ag ₂ S – Silver
Figure 5-12 Effects of Temperature – Copper Corrosion Results after Exposure 6 Days
(Coulometric Reduction)
Figure 5-13 Effects of Temperature – Silver Corrosion Results after Exposure 6 Days (Coulometric
Reduction)
Figure 5-14 Effect of Temperature - Ratio of the Corrosion Product Cu ₂ O – Copper102
Figure 5-15 Effect of Temperature - Ration of the Corrosion Product Ag_2S – Silver102
Figure 5-16 Change of Color for Copper and Silver after Exposure 30 Days under 21°C 50%RH
$NO_2 + SO_2 + O_3 + Cl_2 + H_2S$
Figure 5-17 Change of Color Index over Exposure Time for Copper and Silver under 21°C 50%RH
$NO_2 + SO_2 + O_3 + Cl_2 + H_2S$
Figure 5-18 Images for Copper and Silver Coupons after Exposure 6 Days under 21°C 50% RH
$(MFG: NO_2+SO_2+O_3)$
Figure 5-19 Images for Copper and Silver Coupons after Exposure 6 Days under 21°C 80% RH
$(MFG: NO_2 + SO_2 + O_3)$
Figure 5-20 Images for Copper and Silver Coupons after Exposure 6 Days under 28°C 50% RH
$(MFG: NO_2 + SO_2 + O_3)$
Figure 5-21 Effects of Pollutants Mixture – Copper RGB Values after Exposure 6 Days (Color
Index)110
Figure 5-22 Effects of Pollutants Mixture – Silver RGB Values after Exposure 6 Days (Color Index)
Figure 5-23 Images of Copper and Silver Coupons after Exposure 6 Days under Different
Temperatures (MFG: $NO_2+SO_2+O_3$)
Figure 5-24 Effects of Temperature – Copper RGB Values after Exposure 6 Days (Color Index)
Figure 5-25 Effects of Temperature – Silver RGB Values after Exposure 6 Days (Color Index)
Figure 5-26 Regression of Color Index to Corrosion Thickness (RGB in this figure is the RGB
difference between the clean coupon and the exposed sample)114
Figure 5-27 Images of Copper and Silver Coupons after Exposure 6 Days at 50% RH (left) and
80% RH (right) (MFG: NO ₂ +SO ₂ +O ₃)115
Figure 5-28 Effects of Relative Humidity – Copper RGB Values after Exposure 6 Days116
Figure 5-29 Effects of Relative Humidity – Silver RGB Values after Exposure 6 Days (Color
Index)
Figure 5-30 Copper a) Secondary (Left) and b) Backscattered (Right) Electron Micrographs of the
Top Region at High Magnification (8.5kX)
Figure 5-31 Copper Backscattered Images from which the Following EDS Analysis was
Performed (21°C 50% RH NO ₂ +SO ₂ +O ₃ +H ₂ S+Cl ₂ Exposure 25 Days)119
Figure 5-32 Copper EDS Map of Figure 5-19 (21°C 50% RH NO ₂ +SO ₂ +O ₃ +H ₂ S+Cl ₂ Exposure 25
Days)
Figure 5-33 Copper Backscattered Images from which the Following EDS Analysis was
Performed (21°C 50% KH NO ₂ +SO ₂ +O ₃ +H ₂ S+Cl ₂ Exposure 25 Days)120
Figure 5-34 Copper EDS Map of Figure 5-30 (21°C 50% RH NO ₂ +SO ₂ +O ₃ +H ₂ S+Cl ₂ Exposure 25
Days)121
Figure 5-35 Effects of Pollutants Mixture - SEM/EDS (Copper, MFG: NO ₂ +SO ₂ +O ₃)122

Figure 5-36 Effects of Pollutants Mixture - SEM/EDS (Silver, MFG: NO ₂ +SO ₂ +O ₃)	122
Figure 5-37 Effects of Temperature - SEM/EDS (Copper, MFG: NO ₂ +SO ₂ +O ₃)	123
Figure 5-38 Effects of Temperature - SEM/EDS (Silver, MFG: NO ₂ +SO ₂ +O ₃)	124
Figure 5-39 Effects of Relative Humidity - SEM/EDS (Copper, MFG: NO ₂ +SO ₂ +O ₃)	125
Figure 5-40 Effects of Relative Humidity - SEM/EDS (Silver, MFG: NO ₂ +SO ₂ +O ₃)	126
Figure 5-41 Effects of Pollutants Mixture - Surface Geometry for Copper and Silver Coupc	ons after
Exposure 6 Days (AFM)	127
Figure 5-42 Effects of Pollutants Mixture – Surface Roughness for Copper and Silver C	Coupons
after Exposure 6 Days under 28 C and 50% RH (AFM)	128
Figure 5-43 Effects of Temperature – Surface Geometry for Copper and Silver Coupo	ns after
Exposure 6 Days (AFM)	129
Figure 5-44 Effects of Temperature - Surface Roughness for Copper and Silver Coupo	ns after
Exposure 6 Days under NO ₂ +SO ₂ +O ₃ (AFM)	130
Figure 5-45 Effects of Relative Humidity – Surface Geometry for Copper Coupons after E	xposure
6 Days (AFM, MFG: NO ₂ +SO ₂ +O ₃)	131
Figure 5-46 Effects of Relative Humidity – Surface Roughness for Copper and Silver C	Coupons
after Exposure 6 Days under NO ₂ +SO ₂ +O ₃ (AFM)	132
Figure 5-47 Depth Profile for Cu Element (Copper)	133
Figure 5-48 Depth Profile for C Element (Copper)	134
Figure 5-49 Depth Profile for O Element (Copper)	134
Figure 5-50 Depth Profile for S Element (Copper)	135
Figure 5-51 Depth Profile for Cl Element (Copper)	135
Figure 5-52 Effect of Voltage Bias – Picture	149
Figure 6-1 Schematic Diagram of Oxidation (Shackelford, 1992)	166
Figure 6-2 A Schematic Representation for the Six Regimes and the Transitio	ns and
Transformation (Grardel, 1996)	169
Figure 6-3 A Schematic Diagram of the Basic Elements in the GILDES Model for the C	Gaseous
Regime (Grardel, 1996)	170
Figure 6-4 Schematic of the Formation of Calcareous Deposits in the Diffusion Layer	and 1D
Geometry (Sun, et al., 2012)	177
Figure 6-5 Changes of the Thickness and Growth Rate of Calcareous Deposits with Time	(Sun, et
al., 2012)	177
Figure 6-6 Corrosion of a Metal Surface under a Thin Oxide Film Filled with Moisture	and of
Thickness (L) (Venkatraman et.al., 2011)	178
Figure 6-7 Corrosion Mechanism (Venkatraman et.al., 2011)	179
Figure 6-8 Corrosion Rate Varied with the Thickness of Oxide Product (Venkatraman et.al	., 2011)
	179
Figure 6-9 Effect of Porosity of Oxide (Venkatraman et.al., 2011)	180
Figure 6-10 Effect of Oxide Conductivity (Venkatraman et.al., 2011)	180
Figure 6-11 Cuprite and Brochantite Deposition on Copper (Clarelli, Filippo, & Natalini	i, 2014)
	181
Figure 6-12 Cuprite and Brochantite Theoretical Growth (in Time) on Copper (Clarelli, 1	Filippo,
	182
Figure 0-13 Schematic of Copper Sulfidation Model (Larson, 2002)	183
Figure 0-14 Fit to Copper Sulfidation Rate Data. Points were experimental measureme	nts and
curves were from the model. (a) 400, (b) 200, and (c) 40 ppb (Larson, 2002)	183

Figure 6-15 Schematic of the Corrosion System Modeled: (a) Chemical Species Transfer; (b)
Current Density and Electron Migration
Figure 6-16 History of Studying the Diffusion through the Porous Media (Kantzas, Bryan, &
Taheri)196
Figure 6-17 Regression for Modified Chris' Data under 25 C and 1.9 ppb Cl ₂ 201
Figure 6-18 Model Implementation
Figure 6-19 Relative Humidity Effect on Copper – Corrosion Results after Exposure 10 Days
under 2 μ g/cm ² Cl ⁻ at 25 C (studied by Chen, et al.)
Figure 6-20 Normalized Data and Linear Regression for Corrosion Development under Different
Conditions after 6 Days Exposure
Figure 6-21 Corrosion Development for Modified Data with Cl_2 only at 25 $\ensuremath{\mathcal{C}}$ and 50% RH
(Reference Case)
Figure 6-22 Effects of Relative Humidity – Corrosion Results under Different Relative Humidity
with Cl_2 only at 25 C
Figure 6-23 Effects of Temperature with O ₃ +NO ₂ +SO ₂ + H ₂ S +Cl ₂ at 50% RH216
Figure 6-24 Effects of Temperature with O ₃ +NO ₂ +SO ₂ +Cl ₂ at 50% RH216
Figure 6-25 Effects of Multiple Pollutants at 25°C and 50% RH
Figure 8-1 Possible Expansion of the Recommended Thermal Envelope for Data Centers Where
Cl ₂ and H ₂ S are not Present (as represented by the dashed envelope) (ASHRAE, 2015)226

List of Tables

Table 2-1 Typical Range of Outdoor Pollutants Worldwide (ASHRAE RFP 1755-TRP)	6
Table 2-2 Contaminant Concentrations versus Severity Levels (ANSI/ISA-71.04, 2013)	7
Table 2-3 Unit Conversion	10
Table 2-4 Unit Conversion	12
Table 2-5 Summary of Gaseous Contaminants NO ₂ , O ₃ , H ₂ S, Cl ₂ , and SO ₂ Levels	21
Table 2-6 Limitation of Gaseous Contaminants for IT Equipment	23
Table 2-7 "Realistic" Indoor Worst-case Concentration Levels	23
Table 2-8 Gaseous Properties	35
Table 3-1 Relative Humidity and Temperature Sensor	64
Table 4-1 Measured Pressure Drops, Flow Rates and Air Velocities for the Exposure Cha	ambers
	70
Table 4-2 Uniformity of Pollutants' Concentration	70
Table 4-3 "Realistic" Indoor Worst-case Concentration Levels	73
Table 4-4 Summary for Test Conditions	73
Table 5-1 Experiment Condition for Relative Humidity Fluctuation	143
Table 6-1 Non-dimensional Parameters	190
Table 6-2 Fitting Parameters of Equation (33) for the Diffusion Coefficients for OH Radica	al197
Table 6-3 Parameters Used in the Model	201
Table 6-4 Calculation of Mean Ratio of Corrosion Thickness	206
Table 6-5 Temperature Conversion (Cl ₂ only under 50% RH)	207
Table 6-6 Ratio among Different Pollutant Mixtures under Different Temperature	207
Table 6-7 Corrosion Results under Different Relative Humidities (Based on the Reg	ression
Relationship of Study by Chen et. al)	208
Table 6-8 Ratios of Corrosion Thickness under Different Exposure Conditions	209
Table 6-9 Corrosion Development under Different Thermal Conditions	209
Table 6-10 Calculation for Correction Coefficients R of Current Density	212

1. Introduction

Data centers have the highest energy usage intensity among all building types and consume increasingly more energy due to the consumption of significantly more computing power/performance worldwide. In an effort to reduce energy consumption, an increasing number of data centers have adopted air-side economizers to enable "free-cooling". However, this runs the risk of introducing gaseous and particulate pollutants from the atmospheric environment and causing damage to the information technology equipment (ITE) in the data center due to corrosion to copper and silver materials in the ITE components such as Printed Circuit Boards (PCBs) and silver-containing soldering materials. The present research addresses the impacts of typical gaseous pollutants such as SO₂, NO₂, H₂S, O₃, and Cl₂ under various temperature and humidity conditions.

The reliability of datacom equipment is affected by the thermal and air quality conditions in the data center environment. The existing guidelines for the design and operation of data center environment take the conservative approach by limiting the corrosion level of standard copper and silver coupons after a 30-day exposure to be below 200 Angstroms to 300 Angstroms in the field, respectively. But there is no tool available to predict if this limit would be exceeded for given pollution and thermal environmental conditions at design stage (ASHRAE, 2015). The purposes of this research were to gather new data and investigate the effects of moisture content, temperature and pollutions on the corrosion through laboratory experiments, and to improve the understanding of the corrosion mechanisms through a corrosion model for predicting the corrosion development

under different pollutions and thermal environmental conditions. The findings will enable the assessment of the risk to datacom equipment and potentially allow the operation of datacom equipment under a wider range of temperature and humidity conditions when contamination is low to reduce the energy consumption for air conditioning the data centers.

1.1. Background

There are three conditions which can lead to datacom equipment failures: (1) the polluted environment including corrosive particles and/or gases, (2) the combination of pollutants and an environment having a high relative humidity, and (3) the materials used in the IT equipment being more susceptible to the corrosive gases and particles by design due to other safety concerns (e.g., avoiding the use of lead). There are many ways in which outdoor pollutant gases can enter the building, such as free-air cooling without proper gas filters, makeup air, and air exchanges from leaks in the buildings. Even though there are generally filters in the HVAC systems of data centers, particulate and gaseous contaminations can still enter the data centers to damage the IT equipment due to limited filtration efficiencies. On the thermal side, uncontrolled free cooling can lead to a high and wide range of variation of relative humidity levels in the data center. Regarding the impacts of material selection, directive 2002/95/EC of the European Parliament and of the Council of 27 January 2003 on the Restriction of the use of Certain Hazardous Substance (RoHS) on Electrical and Electronic Equipment eliminated the use of lead in electronic equipment. These requirements have resulted in redesigned IT equipment and modified manufacturing processes, which have made IT equipment more vulnerable to corrosion due to particulate and gaseous

contaminations. Because of these factors, it is important to have more stringent control of the pollutant level in the data center environment.

However, gaseous contamination limits for the reliable operation of electronic equipment and cannot be specified presently in terms of the concentrations of gaseous contaminants in the air due to lack of data on the severity of the corrosion effects under realistic concentration levels and thermal environmental conditions. Information technology equipment (ITE) is allowed to operate for short periods in a wide range of thermal environmental conditions including relative humidity levels up to 90% according to the current standard guidelines (ASHRAE, 2015). There is clearly a need to determine the allowable temperature and relative humidity limits given the pollutant levels that are realistic in the environments around the world for the data center environment, especially under higher relative humidity conditions.

1.2. Objectives and Scope

The objective of the present research was to obtain new experimental data and develop a corrosion model to predict the effects of temperature, relative humidity, and pollutants' levels on copper and silver. The specific tasks included:

 Performing a detailed literature review to understand the importance of field variables – such as temperature, relative humidity and moisture content, air velocity, and pollutant concentration – in order to properly design the experiments, as well as understand the existing corrosion models including the empirical and mechanistic models.

- 2) Developing a mixed flowing gas (MFG) test system and the experimental method for testing the standard copper and silver coupons and printed circuit board (PCB) under the "realistic indoor worst case" scenarios of data centers.
- 3) Designing and performing the experiments to determine how changing the relative humidity or temperature, fluctuating the relative humidity, and applying electrical voltage on the tested PCBs would affect the corrosion of materials when they are exposed to different combinations of air pollutants including SO₂, NO₂, H₂S, O₃, and Cl₂.
- 4) Developing the mathematical model based on corrosion mechanism and related parameters used for different thermal conditions and pollutant levels, and validating the model's ability to predict the corrosion tendency by using normalized laboratory data under realistic pollution levels.
- Based on the results of this research, proposing recommendations to be considered in future revisions of the ASHRAE environmental design guidelines for data centers located throughout the world.

1.3. Organization of this Dissertation

In the next Chapter, a literature review of previous work on the subject is presented with a focus on pollutant levels and thermal conditions in data center, corrosion mechanism, and major influencing factors. Chapter 3 and chapter 4 present experimental setup and facilities, test specimens, experimental method and design, verification of test conditions, and techniques used for evaluating the corrosion results.

Chapter 5 presents and discusses experimental results on copper and silver corrosions obtained by using color index, coulometric reduction, SEM/EDS, AFM, and XPS.

Chapter 6 presents the development of a mechanistic corrosion model, including a literature review of existing empirical and mechanistic models, descriptions of the model developed (including the governing equations, boundary conditions, initial conditions, and related parameters), and comparisons of the model predictions with the experimental results.

Chapter 7 provides a summary of the major conclusions from the study and identifies the specific areas recommended for further investigations. It also includes some recommendations for the operation of data center environment.

2. Literature Review

2.1. Gaseous Pollutant Levels and Thermal Conditions in Data Center Environment

2.1.1. Pollutant Levels

Measured indoor concentrations of the five pollutants of interest (H_2S , NO_2 , SO_2 , Cl_2 , and O_3) in data centers are very limited. In order to define the "realistic indoor worst case" concentrations, we reviewed the available data found in outdoor air and the threshold values defined in relevant standards to provide more insight. In the worst case in which building HVAC systems do not have effective filters, the indoor levels can be as high as the outdoor levels, or even higher than outdoors if indoor sources exist.

ASHRAE 1755-TRP (2015) lists the typical range of outdoor levels of gaseous contamination worldwide (Table 2-1). The International Society of Automation (ISA) Standard (ANSI/ISA-71.04, 2013) classified the pollutant levels of commonly encountered gaseous contaminants in terms of their potential levels of severity in affecting the IT equipment (Table 2-2).

	Outdoor Ranges in				
	Minimum Maximum				
H_2S	4	1400			
NO ₂	5	80			
SO_2	4	40			
Cl ₂	1	10			
03	5	60			

Table 2-1 Typical Range of Outdoor Pollutants Worldwide (ASHRAE RFP 1755-TRP)

		G1 (Mild)	G2 (Moderate)	G3 (Harsh)	GX (Severe)		
	Gas		Gas Concentration (in ppb)				
	H_2S	< 3	< 10	< 50	50		
Group A	SO_2, SO_3	< 10	< 100	< 300	300		
	Cl ₂	< 1	< 2	< 10	10		
	NO _x	< 50	< 125	<1250	1250		
Group B	HF	< 1	< 2	< 10	10		
	NH ₃	< 500	< 10,000	< 25,000	25,000		
	O ₃	< 2	< 25	< 100	100		

Table 2-2 Contaminant Concentrations versus Severity Levels (ANSI/ISA-71.04, 2013)

It is interesting to note that the minimum levels listed by ASHRAE 1755-TRP are slightly higher (but in the same order of magnitude) than the threshold values of the G1 (mild) level for H_2S , Cl_2 , and O_3 , but lower than the G2 (moderate) level. However, for SO₂ and NO₂, the minimum outdoor concentrations listed in ASHRAE 1755-TRP are lower than the G1 (mild) threshold level for corrosion. The maximum levels listed by ASHRAE 1755-TRP are between the G1 and G2 levels for SO₂ and NO₂, between the G2 and G3 levels for Cl₂ and O₃, and exceedingly higher even than the GX (severe) level for H_2S . The comparison suggests that the levels suggested in ASHRAE 1755-TRP are in the range of the guideline limits for corrosion control suggested by the ISA standard with the exception of H_2S , but they correspond to different corrosion levels for different compounds. In order to better understand the levels of the pollutant concentrations that are typically experienced by data centers, we searched literature and contacted researchers in the area of both indoor and outdoor air quality. Results are presented in the following sections.

2.1.1.1. O₃, NO₂, and SO₂ Concentration Levels in the U.S.

As shown in Figure 2-1, the average outdoor O_3 concentrations were between 67 and 88 ppb, which is slightly higher than the maximum value (60 ppb) suggested in the ASHRAE 1755-TRP. The NO₂ levels reduced gradually over the 15 years' period. They ranged between 45 and 65 ppb, which is slightly lower than the maximum value (80 ppb) suggested in ASHRAE 71755-TRP. There has been more significant overall reduction of SO₂ levels in the U.S. since 2001. The average concentration ranged from about 25 to 86 ppb, which is close to the maximum level suggested by ASHRAE 1755-TRP (40 ppb). Therefore, the maximum levels suggested by ASHRAE 1755-TRP are reasonable representations of the average concentrations across the U.S. for O₃, NO₂, and SO₂.



Figure 2-1 2000 – 2015 Pollutant Air O₃, NO₂, and SO₂ Concentration in the U.S. (Retrieved September 2016 from https://www.epa.gov/air-trends/nitrogen-dioxide-trends)

2.1.1.2. SO₂ Concentration Levels Worldwide

Buchard et al. (Buchard, et al., 2014) gave the worldwide SO₂ surface concentration for January and July 2010 (Figure 2-2). The pollutant levels are generally higher in winter (January) than in summer (July), and there are hot spots (highly contaminated regions) in China, India, and U.S. with a maximum level of about 40 ppb, which is consistent with the findings shown in Figure 2-2, and the same given by ASHRAE 1755-TRP.



Figure 2-2 Goddard Earth Observing System Version 53GEOS-5/GOCART Monthly Mean of SO₂ Surface-Level (Revised Run) for January and July 2010 (Buchard et al. 2014)

2.1.1.3. NO2 and SO2 Concentration Levels for Selected Cities

Ranjeet S Sokhi (Sokhi R. , March 2012) collected annual concentrations of NO₂ (Baldasano, Valera, & Jimenez, 2003) and SO₂ for selected cities (Figure 2-3). Maximum levels are greater than 43 ppb (80 μ g/m³) and 19 ppb (50 μ g/m³) for NO₂ and SO₂, respectively. These are slightly higher than the maximum values suggested by ASHRAE 1755-TRP, but in the same order of magnitude. (Hint: the unit conversion is shown in Table 2-3).

Pollutant	$\mu g / m^3$	ppb	Pollutant	$\mu g / m^3$	ppb	
NO ₂	20	10.6		5	1.91	
	40	21.3	SO ₂	10	3.82	
	60	31.9		20	7.63	
	80	42.6		50	19.08	
Note: At 25°C, an ambient pressure of 1 atmosphere						

Table 2-3 Unit Conversion





Figure 2-3 Outdoor Levels of NO₂ and SO₂ for Selected Cities (World Health Organization, 2000)

2.1.1.4. O₃, NO₂, and SO₂ Concentration Levels in Europe

From the European Environment Agency, there are some maps (Figures 2-4, 2-5, and 2-6 below) which show the annual mean concentrations of SO_2 , NO_2 , and O_3 in Europe based on daily averages with at least 75% of valid measurements, in μ g/m³. They are similar to the levels found in the U.S. except somewhat higher O_3 levels were found in certain parts of the Europe. The U.S. has a higher limit set for ozone than Europe. (Hint: in Table 2-4, it shows the unit conversion)

Pollutant	µg/m³	ppb	Pollutant	µg/m³	ppb	Pollutant	µg/m³	ppb
NO ₂	20	10.6		5	1.91	O 3	80	40
	30	16.0	SO ₂	10	3.82		100	50
	40	21.3		20	7.63		120	60
	50	26.6		25	9.54		140	70
Note: At 25°C, an ambient pressure of 1 atmosphere								

Table 2-4 Unit Conversion



Figure 2-4 Annual Mean Concentration of SO₂ (µg/m³) in Europe (EEA) (Retrieved September 2016 from https://www.eea.europa.eu/)



Figure 2-6 Annual Mean Concentration of NO₂ (µg/m³) in Europe (EEA) (Retrieved September 2016 from https://www.eea.europa.eu/)



Figure 2-5 Annual Mean Concentration of O_3 (μ g/m³) in Europe (EEA) (Retrieved September

2016 from https://www.eea.europa.eu/)

2.1.1.5. O₃, NO₂, and SO₂ Concentration Levels in India

Figure 2-7 shows the concentrations of NO_2 , O_3 , and SO_2 in Delhi, India from 2006 to 2016. The NO_2 levels ranged from about 24 to 88 ppb, which are similar to the levels found in the U.S. (45 to 65 ppb, Figure 2-1). The SO_2 levels ranged from 2 to 15 ppb in Delhi, which are less than the average levels in the U.S. (25 to 86 ppb). The O_3 levels in Delhi ranged from 12 to 25 ppb, which are also less than the average levels in the U.S. (67 to 88 ppb).



Figure 2-7 NO₂, O₃, and SO₂ Concentration in Delhi, India from 2006 to 2016 (Retrieved

September 2016 from http://www.cpcb.gov.in/CAAQM/frmCurrentDataNew.aspx?StationName=MPCB)

2.1.1.6. O₃, NO₂, and SO₂ Concentration Levels in Beijing

Figure 2-8 shows test locations (Ding Ling, Huairou Town, Changping Town, Shunyi New Town, Gu Cheng, Olympic Center, Wan Liu, Guan Yuan, Agriculture Exhibition Hall, Dong Si, Wan Shou, Temple of Heaven) in Beijing, China (Zhang, Y. 2016, personal communication). Figure 2-9 through Figure 2-15 show the NO₂, O₃, and SO₂ concentration levels in Beijing, China. O₃ concentrations are higher in summer than winter months, but NO₂ and SO₂ are generally higher in winter than summer months due to the coal burning for heating. The levels of NO₂ and O₃ in Beijing in many cases are double the levels in the U.S., but the SO₂ levels are at a similar level.



Figure 2-8 Test Locations in Beijing, China (Baidu Map)



Figure 2-9 2014 Outdoor Pollutant Levels in Shunyi New Town, Beijing, China (Zhang, 2016)



Figure 2-10 2014 Outdoor Pollutant Levels in Wan Liu, Beijing, China (Zhang, 2016)



Figure 2-12 2014 Outdoor Pollutant Levels in Changping Town, Beijing, China (Zhang, 2016)



Figure 2-11 2014 Outdoor Pollutant Levels in Ding Ling, Beijing, China (Zhang, 2016)



Figure 2-13 2014 Outdoor Pollutant Levels in Dong Si, Beijing, China (Zhang, 2016)



Figure 2-14 2014 Outdoor Pollutant Levels in Temple of Heaven, Beijing, China (Zhang, 2016)



Figure 2-15 2014 Outdoor Pollutant Levels in Wan Shou, Beijing, China (Zhang, 2016)

2.1.1.7. Summary for the Pollutant Levels

Table 2-5 is a summary of information documented above on the concentration levels of gaseous contaminants at various locations in the world. Data for NO₂, O₃, and SO₂ suggest that outdoor concentration levels vary by locations. Beijing had the highest maximum concentrations of NO₂, SO₂, and O₃. Delhi, India had the second highest maximum concentration of NO₂, but its SO₂ and O₃ concentration levels were lower than those reported for the U.S. The pollutant levels of NO₂, SO₂, and O₃ in the Europe are slightly lower than those in the U.S. The third- and second-to-last rows of Table 2-5 show the maximum and the average of the maximum and minimum values of concentrations obtained from the different literature sources, while the last row shows our experiment pollutant levels. If the average of the minimum values and the average of the maximum values are used to represent the realistic range of outdoor concentrations, NO₂, O₃, and

 SO_2 would range between 45-108 ppb, 67-137 ppb, and 25-47 ppb, respectively. These "representative" ranges compare favorably with the maximum values in ASHRAE 175-TRP for NO_2 (80 ppb), O_3 (60 ppb), and SO_2 (40 ppb), which we adopt as the "realistic indoor worst case" concentration levels for the mixed flowing gas tests in the current research.

Measured data for H_2S and Cl_2 are, however, too limited to draw a concrete conclusion. For natural and unpolluted sites, the concentration of H_2S is typically very low (about 0.1 to 2 ppb level) but can reach several orders of magnitude higher near industrial sites (up to 10^7 ppb). The level of Cl_2 in natural and unpolluted outdoor environment is also low (at 0.1 to 0.58 ppb level from the limited data found). However, its concentration can increase indoors if bleach is heavily used. In light of too limited measured field data for H_2S and Cl_2 , one may consider that the threshold concentrations for the G2 (moderate) level corrosion listed in ANSI/ISA-71.04-2014 as the "realistic worst case" concentration (i.e., 10 ppb and 2 ppb for H_2S and Cl_2 , respectively) for data centers. These are lower than the maximum values suggested in ASHRAE 175-TRP (1400 ppb and 10 ppb for H_2S and Cl_2 , respectively), but are sufficiently high to cause significant corrosion based on previous laboratory tests (C. O. Muller, 1990).
Area	NO ₂	(ppb)	O3 (]	opb)	SO ₂ ((ppb)	H ₂ S (ppb)	Cl ₂ (ppb)	
	max	min	max	min	max	min	max	min	max	min
Delhi, India ¹	88	24	25	12	15	2	-	-	-	-
All, USA ²	65	45	88	67	86	25	-	-	-	-
Long Island, NY, USA ³	-	-	-	-	-	-	-	-	0.15	<0.016
Irvine, CA, USA ³	-	-	-	-	-	-	-	-	0.02	<0.0025
La Jolla, CA, USA ³	-	-	-	-	-	-	-	-	0.028	<0.003
Shunyi New Town, Beijing, China⁴	99	0	165	0	47	0	-	-	-	-
Wan Liu, Beijing, China⁴	119	0	135	0	37	0	-	-	-	-
Changping Town, Beijing, China ⁴	104	0	174	0	49	0	-	-	-	-
Huairou Town, Beijing, China⁴	92	0	170	0	46	0	-	-	-	-
Ding Ling, Beijing, China 4	93	0	171	0	31	0	-	-	-	-
Guan Yuan, Beijing, China⁴	122	0	141	0	87	0	-	-	-	-
Temple of Heaven, Beijing, China⁴	98	0	135	0	43	0	-	-	-	-
Gu Cheng, Beijing, China ⁴	119	0	165	0	33	0	-	-	-	-
Dong Si, Beijing, China⁴	126	0	127	0	45	0	-	-	-	-
Olympic Center, Beijing, China ⁴	152	0	134	0	43	0	-	-	-	-
Wan Shou, Beijing, China⁴	116	0	139	0	40	0	-	-	-	-
Agriculture Exhibition Hall, Beijing, China⁴	124	0	149	0	53	0	-	-	-	-
Reykjavik, Iceland ⁵	11.348 (mean)		19.389 (mean)		0.647 (mean)		2.256 (mean)		-	-
European (EEA)6	>27	<11	70	<40	10	<2	-	-	-	-
World (GEO-5) ⁷	-	-	-	-	42	-	-	-	-	-

Table 2-5 Summary of Gaseous Contaminants NO2, O3, H2S, Cl2, and SO2 Levels

World Atlas of Atmospheric Pollution ⁸	>43	<11	-	-	>21	<3	-	-	-	_	
WHO ^{9,10}	48	11	35	20	21	7	8310008	0.101	-	-	
Eastern Tropical Atlantic ¹¹	-	-	-	-	-	-	-	-	0.035	0.001	
Southeast Texas, USA ¹²	-	-	-	-	-	-	-	-	0.0048	0	
Taiwan, China ¹³	-	-	-	-	-	-	-	-	0.58	<0.005	
Urban Areas, USA ¹⁴	52	22	120	100	6	4					
Urban Areas, Canada ¹⁴	22	16	21	17	6	4					
Urban Areas, Europe ¹⁴	34	2	145	65	94	2					
Maximum	152	45	174	100	94	25	8310008	0.101	0.58	0.001	
Average	84	7	116	17	39	2			0.1		
Our Test Level	8	<u>80</u>		<u>60</u>		<u>40</u>		<u>10</u>		2	

The above range of concentration levels fall within the maximum and minimum of the published guideline limits of gaseous contaminants for IT equipment (Table 2-6). It is important to note that the guideline values are used for contamination control with the assumption that the thermal environment is controlled within a small range of conditions (see next section). They are not adequate for assessing the failure risk of ITEs as the data center can operate under wider range of temperature and humidity conditions (ASHRAE, 2015).

Gas	IEC Standard 60721-3-3 (IEC 2002) (ppb)	GR-63- CORE (Telcordi a 2006) (ppb)	ISA Standard 71.04- 1985 (ISA 1985) (ppb)	One Manufacturer' s Internal Standards (ppb)	Max (ppb)	Min (ppb)
H ₂ S	7	40	3	2	40	2
SO ₂	38	50	10	38	50	10
Cl ₂	35	5	1	-	35	1
NO _x	-	700	50	74	700	50
03	5	123	2	49	123	2

Table 2-6 Limitation of Gaseous Contaminants for IT Equipment

Based on the above review and analysis, we proposed the following concentrations as the "realistic indoor worst-case concentration levels" for the mixed flowing gas tests (Table 2-7).

Table 2-7 "Realistic" Indoor Worst-case Concentration Levels

Gas	H_2S	NO ₂	SO ₂	Cl ₂	O ₃
Concentration (ppb)	10	80	40	2	60

2.1.2. Thermal Environment

ITE can operate in a wide range of thermal environmental conditions including those with higher relative humidity conditions according to the current guidelines (Figure 2-16).

The current guideline gives the recommended temperature and relative humidity envelope: the dew point is from -9 °C to 15 °C. The dry-bulb temperature is from 18 °C to 27 °C and the relative

humidity is less than 60%. There are four allowable environmental classes which allow for short periods of operation of the ITE beyond the recommended limits but within the allowable to enable different environmental control levels of the environmental parameters (dew point, temperature, and RH) particularly for economizer cooling. Under normal operating conditions, data centers are advised to operate in the ASHRAE recommended range. If the recommended thermal environmental envelope of the air entering the IT equipment can be increased, it can decrease the energy required to operate the data center HVAC system.



Figure 2-16 Thermal Environmental Conditions of Air Entering IT Equipment (A1, A2, A3, and A4 represent different environmental envelopes for ITE) (ASHRAE, 2015)

2.2. Fundamentals of Atmospheric Corrosion

In the data center, gaseous contaminations can include SO₂, H₂S, NO₂, Cl₂, and H₂S. 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 (T. E. Graedel, 1996), six regimes can be identified (Figure 2-17): G (gas), I (interface), L (liquid), D (deposition layer), E (electrode regime) and S (solid). The study of the 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.



Figure 2-17 A Schematic Representation of the Six Regimes and the Transitions and Transformations (T. E. Graedel, 1996)

In this model, for the gas regime, pollutant gases by convection or detrainment from the interface get into this regime. Then some of the gases deposit on the interface. Some species have chemical interactions with each other. When they arrive at the interface, some of them will volatilize into the gas regime and some will enter into the liquid regime. In the interface regime, there are 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 in each regime. For the species in the solid regime, they react with species which come from the liquid regime and the electrodic regime. The electrodic regime is where electrochemical reaction takes place. Copper loses its electrons and becomes the copper ions which migrate into the electrodic regime. Oxygen which is in the liquid regime reacts with the copper ions to generate depositions. The circle and square symbols in the Figure 2-17 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 (Tran, Fiaud, Sutter, & Villanova, 2003) shows that Cu₂S is an important resistance to diffusion of the ions between the liquid regime and the solid regime.

An electrochemical reaction occurs at the interface of the material and solution with the creation of cathodic and anodic sides on the metal surface. The anode and cathode reactions in atmospheric corrosion are shown in Equations (2-1) and (2-2):

$$Metal \rightarrow Metal^{n+} + ne^{-}$$
 (anode reaction, metal dissolution) (2-1)

$$\frac{1}{2}O_2 + H^+ + 2e^- \rightarrow OH^-(\text{cathode reaction, oxygen reduction})$$
(2-2)

Figure 2-18 shows a schematic description of the atmospheric corrosion of copper.



Figure 2-18 A Schematic Description of the Atmospheric Corrosion of Copper

Major identified chemical reaction processes shown in Figure 2-18 are:

- 1. $2Cu + O_2 + 2H_2O = 2Cu(OH)_2$; $Cu(OH)_2 = Cu_2O + H_2O$;
- 2. $H_2S + 2O_2 = H_2SO_4;$
- 3. $Cu + H_2SO_4 = CuSO_4 + H_2(g);$
- 4. $H_2S + 2Cu + 0.5O_2 = Cu_2S + H_2O;$
- 5. $Cu^{2+} + 2Cl^{-} = CuCl_2;$
- 6. $SO_2 + H_2O = H_2SO_3;$
- 7. $SO_2 + O_2 + 2e^- = SO_4^{2-}$;
- 8. $2Cu + 2NO_2 + H_2O = Cu_2O(s) + 2HNO_2(g);$
- 9. $Cu_2O + 2NO_2 + 4H^+ = 2Cu^{2+} + H_2O + 2HNO_2(g);$

10. $2NO_2 + H_2O = NO_3 + NO_2 + 2H^+$.

In the case of corrosion of ITE, because the air is strictly controlled to have a dew point lower than the surface temperature of ITE components to avoid 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 adlayer, it results in the formation of chloride ions. And these ions can react with the copper, which causes the copper to dissolve in the liquid regime. Sulfur dioxide reacts with ozone in the liquid regime and ozone oxidizes the sulfur dioxide to H_2SO_4 . Then H_2SO_4 combines with the copper to generate the CuSO₄. NO₂ dissolves in the liquid regime to create HNO₂. It has a reaction between HNO₃ and Cu to result in products of Cu₂O and HNO₂(gas). NO₂ also generates NO₂⁻ and NO₃⁻ after dissolving in liquid. (Processes 5 to 10 above).

While the above potential reaction pass ways can be identified, there is a lack of data and knowledge which pass ways are more pronounced under a given temperature and relative humidity condition. Synergistic effects under the different combinations of pollutants further complicate

the problem and make it very challenging to determine the combined effects of multi-pollutants, temperature and humidity on the corrosion development.

2.3. Factors Affecting the Corrosion Rates of Copper and Silver

Atmospheric corrosion is the deterioration and destruction of material and its vital properties due to electrochemical processes as well as the other reactions on its surface with the constituents of the atmosphere surrounding the material. The important factors in atmospheric corrosion are temperature, relative humidity, exposure pollutant level, and exposure time.

2.3.1. Thermal Environmental Conditions

2.3.1.1. Relative humidity

Concept of critical relative humidity: The primary value of critical relative humidity is the humidity below which no corrosion of the metal in question takes place. The corrosion rate at or just above the primary critical relative humidity (e.g., 60% RH) is very slow. The presence of gaseous pollutants in the atmosphere and subsequent depositions on the surface can lead to a secondary critical relative humidity (e.g., 75-80% RH) at which the corrosion rate increases sharply due to the hygroscopic nature of the corrosion products. In some cases (e.g., with iron or steel), there may be even a tertiary critical humidity (e.g., 90% RH) above which the corrosion rate further increases probably due to capillary condensation of moisture within the oxidizing products (rusts) (Syed, 2006). The primary value of critical RH for uncorroded metals seems to be virtually independent of the type of metals, but the secondary and tertiary (if ones exist) 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).

Many investigations have shown that the water vapor pressure has an influence on the corrosion rate (Vernon, 1931; T. Aastrup et al., 2000; Peter Eriksson et al., 1993; Per Backlund et al., 1966). Vernon (1931) shows that when the relative humidity arrives at a critical relative humidity, it will increase the corrosion rate sharply.

The value of the critical relative humidity depends on the type of pollutants and moisture content (and hence the temperature for the given relative humidity level) in the atmosphere, and the secondary relative humidity depends on the interaction between the rust and moisture (Vernon,



Figure 2-19 Weight Increase due to Corrosion of Iron Specimens under Different Exposure Conditions (W. H. J. Vernon, 1935)

1935). Vernon measured the weight increase due to corrosion of iron specimens under four different atmospheric exposure conditions when the relative humidity was increased from 15% to 90% at 25°C (Figure 2-19).

Curve B had 0.01% SO₂ and relative humidity increased with time. Around 60% relative humidity, the corrosion rate increased sharply on curve B. For curve C, SO₂ was omitted when relative humidity was around 60% (the critical humidity range) at sixteen days. Comparing to curve B, the gradient of corrosion rate was larger than curve B when relative humidity was higher than 60%. So, withdrawing SO_2 led to the increase of the corrosion rate. For curve E, purified air without SO_2 was used, which resulted in a smaller rate of corrosion comparing to curve B, indicating the important role of SO_2 for the corrosion process. Curve B shows that when relative humidity was between 0 to 60%, the difference of the corrosion rate between curve B and curve E was small. So, the influence of water vapor was small when relative humidity was lower than the critical humidity. When relative humidity was higher than the critical relative humidity, water vapor had a large influence on the rate of corrosion when SO₂ was present for at a period of time (Curve C) or throughout (Curve B). Without the presence of SO₂, the corrosion rate increased at a relatively constant pace with the increase of relative humidity without an obvious "critical" value. Comparing curve B to curve P indicates that adding 0.01% CO₂ to the purified air inhibited the corrosion development even when RH was as high as 90%. Figure 2-20 shows the relative behavior of iron, zinc, and copper. At the same condition, the corrosion rate of copper is less than it of iron and zinc at 25°C.



Figure 2-20 Relative Behavior of Iron, Zinc, and Copper (0.01% SO₂, Increasing Humidity in Early Stages) (W. H. J. Vernon, 1935)

2.3.1.2. 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 in fewer water molecules being adsorbed on the material surface, and hence leads to a lower amount of soluble pollutant's deposition on the surface and would likely reduce the corrosion effect. 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. P. S. Mohan et al. (1991) studied the effects of temperature on corrosion of mild steel, zinc, and copper. According to their results, the rate of corrosion at 80% RH and 100% RH at 40 °C was less than that at 35 °C for the zinc which was in 0.1 liters SO₂. But at 60% RH, when the temperature increased, the corrosion at 0.1 liters SO₂. For the copper, at 60% RH for 35 °C and 40 °C, the corrosion rate was more than that at 80% RH

and 100% RH for 35 °C and 40 °C. This exhibited that 60% RH is an important relative humidity. It shows that increasing the relative humidity helps to form the protective layer for copper.

Other researchers (J. P. Franey et al., 1985) also found the influence of temperature on the corrosion rate. They exposed silver to 100 ppm H₂S for five weeks while changing the temperature. Figure 2-21 showed that at lower temperature 21°C and higher temperature 80°C the corrosion products were larger than the middle temperature 42°C. With increasing temperature, the water layer becomes thinner on the silver surface so that the dry sulfidation reaction becomes the main mechanism for corrosion.



Figure 2-21 Variation of Average Film Thickness with Increasing Temperature for the Silvers (J. P. Franey et al., 1985)

These studies show that the effect of temperature on corrosion is complicated. It can either enhance or reduce the corrosion rate depending on the level of relative humidity, temperature, and pollutant levels. More importantly, what is the major corrosion mechanism under the specific hydrothermal and contamination conditions needs to be further studied.

2.3.1.3. Air velocity and turbulence

Air velocity and turbulence will affect the mass transfer between the gas regime and the liquid regime on the surface. The gas concentration in the liquid regime has an influence on the corrosion rate. When increasing the air velocity, the mass transfer coefficient is increased and hence leads to an increase in corrosion rate until the mass transfer rate no longer is the limiting process of corrosion development. In other words, the rate of corrosion can increase with the increasing air velocity until an air velocity above which the corrosion rate plateaus (ASHRAE 2014). For copper and silver corrosion testing, it was suggested that a minimum 0.03 m/s should be maintained to minimize the dependence of corrosion rate (Muller 1990). More research is needed to determine the critical air velocity level above which its effect on the corrosion rate can be neglected. Results of such a study are not only useful for setting the test conditions in chamber studies, but also can guide field monitoring regarding where the test coupons should be placed.

2.3.2. Gaseous Contamination

There are five kinds of gaseous contaminations: O_3 , NO_2 , SO_2 , H_2S , and Cl_2 . Table 2-8 shows the properties of these gases. NO_2 are very soluble in the water at room temperature 20°C. Ozone has a higher solubility than other gases.

Table 2-0 Gaseous Troperties	Table 2-8	Gaseous Pro	perties
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Gas	O 2	O 3	NO2	SO2	H2S	Cl2
Molecular weight (g/mol)	32	48	46	64	34	70
Solubility in water at 20°C (g/100g water)	0.0043	57	Very water soluble	11.28	0.385	0.729

2.3.2.1. Sulfur dioxide

Sulfur dioxide is the most common corrosive gas for the Datacom equipment. Combustion of all fossil fuels forms sulfur dioxide, and the smelting process of metals emits sulfur dioxide. T. Aastrup (2000) has found that 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. Total mass change increased due to introducing SO₂. Cu₂O did not show a significant change, and a distinct change in mass gain kinetics upon SO₂ introduction can be seen in Figure 2-22.



Figure 2-22 Total Mass Gain (T. Astrup et al. 2000)

There are others (Peter Eriksson et al., 1993) that came to the same conclusion in their research. They exposed copper samples to 4.6 ppm SO₂ and pure air at 90% RH for four weeks. The mass of corrosion products with SO₂ exposure was higher than that in the case with just pure air exposure. S. Feliu (2003) exposed copper to 305 ppb ($800 \ \mu g/m^3$) SO₂ at 50% RH for 30 days. The corrosion products increased with exposure time. Muller (1990) performed SO₂ corrosion tests for copper and silver under a more realistic concentration level (29 ppb) under standard chamber test conditions (23°C, 50% RH, and air velocity > 0.03 m/s). He found that the thickness of corrosion product was around 450 Angstroms for SO₂. However, data on the combined effects of SO₂ concentration, RH, and temperature on the copper and silver corrosion rates under low SO₂ concentration in data center environment are lacking.

2.3.2.2. Nitrogen dioxide

Nitrogen dioxide source is the high-temperature combustion and biomass burning. Natural phenomenon like lightening also forms NO₂. According to research results (Peter Eriksson et al. 1993), NO₂ has very small corrosive effects alone even in the ppm range. Their experiment exposed the 99% pure copper to air which contained 90% relative humidity, 0.49 ppm of NO₂ at 22 °C. The exposure time was four weeks with the results displayed in Figure 2-23 where the mass gain of the copper specimens that were exposed to individual SO₂, NO₂, or a mixture of SO₂ and NO₂, respectively. There was no significant difference in mass gain between the pure air and NO₂ exposures. A larger mass gain was measured for the specimen exposed to SO₂ as expected. The specimen exposed to the NO₂ and SO₂ mixture had a much higher mass gain, indicating a synergistic effect between NO₂ and SO₂.\



Figure 2-23 Mass Gain of Copper Samples (Peter Eriksson et al. 1993)

S. Feliu (2003) also studied the effect of NO₂ and/or SO₂ on the corrosion rate. They tested the mass gain of the copper when copper was exposed to 426 ppb (800 μ g/m³) NO₂ at 50% RH for 30

days. With increasing exposure time, the mass gain of copper increased. Muller (1990) found similar results for copper. NO₂ had little influence on the corrosion rate of copper.

The data reviewed above indicate that NO_2 alone is not a significant factor for corrosion, but it can accelerate corrosion through synergistic effect with SO_2 . Data on its possible synergistic effect with other gases of interest such as O_3 , H_2S , and Cl_2 under different humidity and temperature conditions are lacking in the literature.

2.3.2.3. Hydrogen sulfide

Hydrogen sulfide is one of the most important gaseous contaminants in the data center. It can cause serious corrosion on a printed 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 hardware type components 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. For the PCBs, the sulfur-bearing gases cause creep sulfide corrosion products on the PCBs.

Tran (2003) researched the atmospheric corrosion of copper from hydrogen sulfide. The results showed that hydrogen sulfide had a huge influence on the corrosion of copper. Hydrogen sulfide is corrosive to most metals and alloys. In Tran's (2003) study, copper was exposed to different concentrations of hydrogen sulfide (less than 10 ppb, between 0.1 and 0.5 ppm, and more than 1 ppm) over 77 days. The temperature varied between 15°C and 27 °C, and the relative humidity

varied between 35% and 75%. Figure 2-24 shows how the thickness of the corrosion product Cu_2S varied with time.



High H₂S: > 1ppm
Medium H₂S: 0.1 - 0.5 ppm
Low H₂S: < 10 ppb
Figure 2-24 Variation with Time of the Thickness of Cu₂S during Exposure of Copper at Different H₂S Concentration during Field Test (T. T. M Tran et al. 2003)

After copper was exposed to these conditions, copper sulfide was formed. Exposure to a higher concentration of H_2S resulted in a faster and larger increase in the thickness of Cu_2S , as expected. The data also show that there appears to be a maximum thickness of Cu_2S 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 Cu_2S 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.

2.3.2.4. Ozone

Natural and anthropogenic electrical discharge is the source of the ozone. It can increase the corrosive effect for copper and silver. T. Aastrup (2000) conducted an experiment in which copper samples were first exposed to the air at 80% RH with 200 ppb SO_2 for 180 min, followed by introducing the 200 ppb O_3 at 80% RH (Figure 2-25).



Figure 2-25 Total Mass Gain (T. Aastrup et al. 2000))

It can be seen that the introduction of O_3 had increased the mass change sharply. In other words, O_3 accelerates the corrosive effect of SO_2 on the copper. Other researchers (T. E. Graedel et al., 1984) showed that ozone enhanced copper sulfate. Data on the O_3 corrosion of copper and silver under a more realistic indoor concentration (< 50 ppb) are lacking.

2.3.2.5. Chloride

Chloride has a limited corrosive ability to copper or silver. But it has a large influence on these metals when it combines with hydrogen sulfide. In the study by Muller (1990), the copper and silver were exposed to 1.9 ppb of Cl_2 at 22°C and 50 ± 5% RH for one month. The results (Figure 2-26) show that chloride alone had a mild corrosion effect, similar to that of SO₂ tested, but significantly weaker than that of H₂S. Feliu (1993) reported that chloride ion has an influence on the corrosion of metals. Data are lacking on the synergistic effects of Cl_2 with other gasses, and under different thermal conditions.



Figure 2-26 Corrosion Film Thickness (Muller, 1990)

According to Abbott's research (Abbott, 1988), he defined four classes of mixed gas environments by composition. Class II: 10 ppb H₂S, 10 ppb Cl₂, 200 ppb NO₂, 70% RH, 20°C. Class III: 100 ppb H₂S, 20 ppb Cl₂, 200 ppb NO₂, 70% RH, 30°C. Class IV: 200 ppb H₂S, 50 ppb Cl₂, 200 ppb NO₂, 75% RH, 50°C. Gold and copper were exposed to these environments. His result showed that at class II, chloride was critical for reproducing the corrosion mechanism. The role of Cl₂ was to remove the CuO₂ so that other pollutants can attack Cu directly.

2.3.3. Synergistic Effect

There is an effect arising among multiple pollutant gaseous that causes an effect greater than the simple summation of their individual effects, which is called the synergistic effect. The combined effects of different pollutants and thermal conditions are very complex, and not yet well understood. Data is especially lacking under field pollutant concentration levels which are typically much lower than those used in the laboratory studies. Muller (1990) researched the multiple contaminant gas effects for copper and silver. It gave us a very good view to understand the synergistic effects. Copper and silver coupons were exposed to the air at $50 \pm 5\%$ RH, $22 \pm 2^{\circ}$ C. Their exposure time was one month and the face air velocity across the coupons was 0.03 m/s. Table 2-6 shows the concentrations of the chlorine, hydrogen sulfide, nitrogen dioxide, and sulfur dioxide in Muller's (1990) experiments, and the results are shown in Table 2-7, and are plotted in Figure 2-27 through 2-30.

Contaminant Gas	Concentration Level (ppb)
Chlorine	$1.9 \pm 5\%$
Hydrogen Sulfide	$11 \pm 2\%$
Nitrogen Dioxide	$128 \pm 2\%$
Sulfur Dioxide	29 <u>±</u> 2%

Table 2-6 Concentration Level for Muller's Experiments

Table 2-7 Test Results from Muller (1990)'s Experiments.

	Copper Coupon Test Data												
Note:		e isa	ы.,	a saga	Total Cop	per Corro	sion (in a	ngstroms)		16.54			
Coupon	Cl2	H2S	NO2	SO2	CI2,H2S	CI2,SO2	H2S,NO2	NO2,SO2	CI2, H2S,	CI2, H2S,	CI2,NO2,	H2S,NO2,	CI2,H2S,
No.									NO2	SO2	SO2	SO2	NO2,SO2
3	108	330	153	149	57	129	366	170	317	152	250	283	309
6	127	431	173	153	236	137	525	197	349	273	354	393	367
9	147	531	193	157	414	146	649	223	403	385	434	503	433
12	167	631	212	161	592	155	754	249	479	491	501	612	512
15	187	732	232	165	771	166	845	276	576	593	561	722	606
18	207	832	252	169	949	179	931	302	694	692	614	832	717
21	226	932	271	173	1127	194	1009	329	834	788	663	941	848
24	246	1033	291	176	1306	Ap. 212	1082	355	996	882	709	1051	1004
27	266	1133	311	180	1484	233	1151	382	1179	975	752	1161	1188
30	286	1233	330	184	1662	259	1215	408	1384	1065	793	1270	1406
ISA*	1000	1000	1000	450	2000	1450	2000	1450	3000	2450	2450	2450	3450
(+/-)%	-71%	23%	-67%	-59%	-17%	-82%	-39%	-72%	-54%	-57%	-68%	-48%	-59%
		EXP	ECTED		1480	431	1517	476	1730	1620	654	1566	1766
133	ne salen Sene s	DIFI	ERENC	E (+/-)%	12%	-40%	-20%	i –14%	-20%	-34%	21%	-19%	-20%

	Silver Coupon Test Data													
ER	a with every such that the second second silver Corrosion (in angstroms) and the second second second second se													
Coupon	CI2	H2S	NO2	SO2	CI2,H2S	CI2,SO2	H2S,NO2	NO2,SO2	CI2,H2S,	CI2,H2S,	CI2,NO2,	H2S,NO2,	CI2,H2S,	
No.			Alter and		stander.		2.25.24	71.00	NO2	SO2	SO2	SO2	NO2,SO2	
3	23	39	33	38	33	8	173	25	162	57	150 / 41	206	161	
6	30	60	35	41	68	18	314	33	273	89	51	349	305	
9	37	80	36	43	104	29	446	41	384	115	58	475	423	
12	44	100	38	46	140	40	571	49	495	139	63	590	577	
15	51	121	40	48	175	52	692	57	606	160	68	699	709	
18	58	141	41	51	211	65	810	65	717	181	72	802	839	
21	65	162	43	54	247	77	925	73	829	199	76	902	967	
24	72	182	44	56	282	90	1038	81	940	217	79	990	1903	
27	79	203	46	59	318	103	1149	89	1051	235	82	1091	1219	
30	86	223	47	61	354	116	1258	97	1162	251	85	1181	1343	
		EXF	ECTED	2013 X	309	148	270	109	547	307	118	507	527	
		DIF	FERENCE	(+/-)%	14%	-21%	365%	5 -11%	112%	-18%	-28%	i 133%	5 155%	

* Expected ISA corrosion level



Figure 2-27 Copper Coupon Test Data for Cl₂, H₂S, NO₂, and SO₂ (Muller, 1990)



Figure 2-28 Silver Coupon Test Data for Cl₂, H₂S, NO₂, and SO₂ (Muller, 1990)



Figure 2-29 Copper Coupon Test Data for Synergistic Effect (Muller, 1990)



Figure 2-30 Silver Coupon Test Data for Synergistic Effect (Muller, 1990)

According to the above Figures 2-27 to 2-30, H_2S as a single compound or in combination is the worst corrosive catalyst. For H₂S alone, the corrosive film thicknesses for copper and silver were 1233 Angstroms and 223 Angstroms after 30 days exposure. Also, the combined effect of H₂S and Cl₂ can cause more corrosion on the surface of copper and silver coupons than other gas pairs. When H_2S combined with Cl_2 , the total corrosion thicknesses minus the summations of the corrosion thickness due to individual exposure were 429 Angstroms and 131 Angstroms for copper and silver. For three-gas combinations, Cl_2 , NO_2 , and H_2S the results were higher corrosive levels than any other three-gas combinations. When H₂S combined with Cl₂ and NO₂, the total corrosion thicknesses minus the summations of the corrosion thickness due to individual exposure were 151 Angstroms and 939 Angstroms for copper and silver. With these four gases, Cl₂, H₂S, NO₂, and SO₂, the damage to the metal surface is mostly for silver. In the case of coppers, H₂S damages the metal surface mostly (Figure 2-27). For silver, Cl₂ damages the metal surface mostly compared to other kinds of pollutants (Figure 2-29). According to the limits (Particulate and gaseous contamination in Datacom environments, 2nd ed.), the corrosion rates of copper and silver should be less than 300 Angstroms/month and 200 Angstroms/month, respectively, to prevent equipment failure. When gaseous contaminants include H₂S, the corrosion rates of copper and silver will exceed the current limitations specified by ASHRAE Datacom book on contamination.

Muller's data also indicated that under the relatively low pollutant concentrations tested, effects of individual contaminants were below the 300 Angstroms limit for copper, and 200 Angstroms for silver, but were detectable within the 30-day test period. The combined corrosion effects with multiple gases exceeded the limits. These suggest that the concentration levels chosen for our tests are adequate for mixed flowing gas testing.

Christofer Laygrad (Aastrup, Wadsak, Leygraf, & Schreiner, 2000) noted that NO_2 enhanced the formation of the sulfate ions through a catalytic mechanism, and O_3 enhanced the corrosion process through a stoichiometric reaction. The catalytic mechanism can accelerate the reaction but cannot produce new products. Moreover, the stoichiometric reaction process resulted in additional reaction products as well as increased the reaction rate.

Further studies are needed to quantify the synergistic effects among different contaminants and moisture levels, and to develop a method that can be used to predict the combined effects from test data on individual effects to the extent possible.

2.4. Summary

There are two kinds of pollutant concentrations data: measurement data of outdoor pollutant levels and limitation of gaseous contaminants for IT equipment protection against corrosion (Table 2-7 from Table 2-5 and Table 2-6).

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	94	0	0.58	0	152	0	174	0
Limitation (ppb)	40	2	50	10	35	1	700	50	123	2

Table 2-7 Summary of Pollutant Concentrations

According to ASHRAE Datacom Book (2009), the current guideline gives the recommended temperature and relative humidity envelope: the dew point is from -9°C to 15°C; the dry-bulb temperature is from 18°C to 27°C, and the relative humidity is less than 60%.

In the moist air when the metallic materials are exposed to the environment with gaseous contaminations, their surfaces will be corroded and damaged. Different kinds and levels of contaminants, temperature, relative humidity, and air velocity cause different corrosion on the metallic materials. There are some corrosion products generated by corrosion processes on the surfaces of materials. They can absorb water vapor from the gas regime. After a while, in some cases, the corrosion products themselves can become resistive to the diffusion of ions between the adsorbed moisture layer and the metals.

A primary critical relative humidity exists below which the corrosion effect is insignificant. A secondary critical humidity also exists above which the corrosion rate increases sharply. The critical relative humidity depends on the pollutant type exposed and moisture content as well as the interactions between the moisture and the corrosion products ("rust"). The variation of temperature has an influence on the thickness of the water layer on the surface of metallic materials and the activity of ions, and hence can either increase or decrease the corrosion rate. Air velocity over the surface affects the mass transfer between the gas regime and the liquid regime on the surface of metalls. Gaseous contaminants which are transported between the gas regime and the liquid regime cause different pollutant concentrations in the liquid regime, which affects the corrosion rate of materials. A higher air velocity can increase the corrosion rate until it reaches a level (about 0.03 m/s) above which the corrosion rate levels off when the mass transfer is no longer a limiting process.

Chloride, nitrogen dioxide, and sulfur dioxide are the common corrosive gases for atmospheric corrosive agents. According to the literature review, 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. Hydrogen sulfides and ozone are very important gaseous pollutants in the data center environment. Each of them alone can damage the equipment, and their synergistic effects with the other compounds can cause even more damages. H₂S alone can cause significant corrosion. O₃ can cause significant corrosion only when other pollutants such as SO₂ co-exist. 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.

In the standard laboratory testing with mixed flowing gases, copper and silver specimens are exposed to different pollutants and concentration levels inside an environmental chamber under controlled temperature, relative humidity, airflow rate and air velocity conditions. By changing the factors affecting the corrosion, the effects of the different factors on the corrosion rates can be measured. Several techniques are available to determine corrosion rates and identify the corrosion products including QCM, coulometric reduction, SEM, XPS, FTIR, and EIS.

Even though atmospheric corrosion has been a very important field of study, there are still some knowledge gaps including the lack of experimental data under multiple pollutants mixture on a wider variation range of temperature and relative humidity and with lower (more "realistic") pollutant concentrations. In order to the effective corrosion control, corrosion study needs the feasible method to link experiment tests to the field exposure condition. It also requires a deeper understanding of the synergistic effects and a mechanistic model to predict the corrosion development under different scenarios. In this study, more experimental data were obtained for copper and silver under "realistic" indoor worst-case pollutant concentrations and the effects of temperature from 21°C to 28°C and relative humidity from 50% to 80% were also tested. Besides, based on the experimental results and literature review, a mechanistic corrosion model was developed for cooper with the Cl₂-containing pollutant mixtures, and the normalized experimental data were used for calibrating the mechanistic corrosion model.

3. Experimental Apparatus and Instrumentation

3.1. Test system composition

According to Standard Practice for Conducting Mixed Flowing Gas (MFG) Environmental Test (B827 – 05), a MFG test facility was developed for the present study. It has the capability of monitoring and controlling the thermal environment, air velocity, and contaminant concentration. The test system (Figure 3-1) consisted of the corrosion exposure chambers, a mixing chamber, the gas supply system, and a monitoring reference chamber. It was developed at the Syracuse University Building Energy and Environmental Systems Laboratory (BEESL). Corrosion exposure chambers and a reference exposure chamber were placed into the hood in order to avoid the pollutants diffusing into the lab space, which can be harmful to human health. The main gas supply system was exposed to the lab space (Figure 3-2).



Figure 3-1 Schematic of the Test System (six of the seven corrosion test chambers were used)



Figure 3-2 Photo of the Test System

As shown in Figure 3-1, the building compressed air passed through a pressure regulator and air filter. The mass flow controller controlled the gas quantity into the system and filtered organic particles, pollutants, and organic chemical compositions. One portion of the gas passed into the dynacalibrator and the ozone generator while the other passed through the humidifier. Moist air and all pollutant gases mixed in the mixing chamber and then separated into the six exposure chambers. The remaining moist air passed into a monitoring reference chamber that was used for monitoring the exposure conditions during the experiment. The entire gas supply system used Teflon PTFE tubes to minimize the sorption effect of pollutants. After connecting all the components, the liquid leak detector was used to detect any possible leaks and verify the airtightness of the system.

3.2. Corrosion Exposure Chamber

3.2.1. Exposure Chamber Design

It was important for the MFG test system to have a well-designed exposure chamber for exposing the test specimens/coupons to the pollutants uniformly. At the same time, the main aspects which needed attention included the material of the exposure chamber, the uniformity of the gas which passed over the coupons, the airtightness of the exposure chambers, and the flow rate (in order to avoid a velocity effect). Figure 3-3 shows the exposure chamber in an AutoCAD drawing and the design of the sample holder. Figures 3-4 and 3-5 show photos of the chamber.



Figure 3-3 Schematic Diagram for Exposure Chamber and Sample Holder



Figure 3-4 Actual Exposure Chamber



Figure 3-5 Sample Holder for Coupons

3.2.2. Material and Airtightness

According to ASTM B827-05 (2014), the material of the exposure chamber needs to be nonreactive, low-adsorbing and nonmetallic material. For the airtightness of the chamber, the leak rate should be less than 3% of the volume exchange rate. In order to create the required airtightness,

the exposure chambers were made by a 3D printer, Foamlabs Form2 (Figure 3-6). The printer used clean photopolymer resin to create the chamber models.



Figure 3-6 3D Printer

3.2.3. Uniformity and Flow Rate

In order to satisfy the requirement for the airflow uniformity, two perforated plates and a sufficient entrance length (Figure 3-4) were designed to introduce the fully developed uniform flow into the exposure chamber. The two perforated plates had an open area of 30% of the area of outlet. Abbott's (1988) research showed that when the air velocity over the coupon surface was larger than 5 ft/min, the air velocity effect on the corrosion could be ignored. The cross-section flow area was 4.5 cm by 1.5 cm which resulted in an air velocity of 19 ft/min, which was much larger than the required 5 ft/min. Therefore, the air velocity in the exposure chamber for the present study was considered sufficiently high to have a negligible effect on the corrosion rate.

3.3. Gas Supply System

3.3.1. Total Supply Capacity and Air Source

In order to maintain the proper gas concentration levels of O_3 (60 ppb), NO₂ (80 ppb), SO₂ (40 ppb), H₂S (10 ppb), and Cl₂ (2 ppb), the total supply flow rate was 28 lpm, including 21 lpm for humidifiers, 3 lpm for pollutants (0.0689 lpm for dynacalibrator and 2.95 lpm for ozone generator) and 4 lpm for a reference chamber. The primary gas flow calibrator from UltraFlo was used to calibrate the flow rate. It had an accuracy of $\pm 0.5\%$ of any display. After building up the system, each connection was detected by a snoop leak detector in order to make sure the airtightness for the whole system and supply capacity.

The air source was the compressed dry air from the lab building. As shown in Figure 3-7, the air passed through the lab clean air filter systems before going into the humidifier and pollutant generators (ozone generator and dynacalibrator for NO₂, SO₂, Cl₂, and H₂S). In order to remove the hydrogen sulfide, sulfur dioxide, nitric oxide, and formaldehyde, one part of the air filter consists of chemisorbants (Figure 3-8) from Purifil, which is shown below.


Figure 3-7 Air Supply before the Humidifier and Pollutant Generators



Figure 3-8 Air Filter (Left) with Chemi-sorbent (Right)

After the chemi-sorbent, the compressed air went through the main lab clean air filter system. This system (Figure 3-9) included four key elements from Wilkerson: FRP-96-653 (general purpose filter element, air treatment 5 micron), MTP-96-648 (micro element .01), MXP-96-651 (coalescing filter element which was used to remove oil vapor, water, and other contaminants from a compressed air line), and MXP-96-650 (activated carbon element).



Figure 3-9 Air Filter System

3.3.2. Humidity Source

The compressed air cannot satisfy the requirement of relative humidity for corrosive gas mixture. In order to increase the relative humidity of the pollutant gases, humidification of the supply air was performed bypassing part of the flow through two water impingers (Figure 3-10) connected in series. The water impingers include two tubes, one (gas inlet) inserts into the deionized water and the other (gas outlet) is above the water surface. After clean air enters into the deionized water, it adsorbs the moisture content from the deionized water then exits the impinger at the gas outlet. Deionized water was added daily in order to control the variation of relative humidity to be no more than $\pm 3\%$ RH. The materials of the water impingers were clear polycarbonate. The volume of each impinger was 7 L. The humidification unit can generate 50% RH without any heater. For higher than 70%RH, an air heater was used to heat the water to allow more water to evaporate into the supply air stream.



Figure 3-10 Water Impingers for Controlling Relative Humidity

3.3.3. Temperature Control

There were two test temperatures in this study, 21°C and 28°C. For 21°C, the whole mixing flow gas system was exposed to the lab environment. So, the exposure temperature was controlled by the temperature of the lab space within \pm 1°C, which had its own HVAC system. For 28°C, the mixing chamber and exposure chambers were put into an insulated small stainless-steel chamber. A heat strip and a fan were placed inside the chamber, and a PID controller and a thermocouple were used to control the temperature of the air inside the stainless-steel chamber at 28°C within \pm 1°C.

3.3.4. Corrosive Gas Source

3.3.4.1.Ozone generator

In this study, a UV lamp in the supply air stream was used for ozone generation with the calibration of ozone monitor from 2B Tech. Model 202 (Figure 3-11). Its range was from 1.5 ppb to 250 ppm

and resolution was 0.1 ppb with the accuracy of 1.5 ppb or 2% of reading. The limit for detection of this instrument is 3.0 ppb.



Figure 3-11 Ozone Generator (Left) and 2B Tech. Model 202 Ozone Monitor (Right)

3.3.4.2. Permeation tubes and dynacalibrator for NO₂, SO₂, H₂S, and Cl₂

In order to produce the target concentrations of pollutants, three permeation tubes (H_2S , NO_2 , and SO_2) and one wafer were purchased. Dynacailibrator (Figure 3-12) is a Dynacal® permeation device to generate and deliver precise concentrations ranging from ppb to high ppm for hundreds of different compounds. They were placed inside the temperature-controlled gas emission chamber of the dynacalibrator. The temperature of gas-emission chamber was maintained at 30°C. Table 3-1 lists the operating parameters for pollutant gas generation.



Figure 3-12 Permeation Tubes for NO₂, SO₂, H₂S, and Cl₂

Chemical Name	H_2S	NO ₂	SO ₂	Cl ₂
Target Ci, ppb	10	80	40	2
Target Ci, ng/L (= µg/m ³)	14	151.2	105.2	3.96
Required Generation rate mi, ng/min,	336	3628.8	2524.8	95.04
Permeation exit Cgi (µg/m³) at 0.075 lpm	4480.0	48384.0	33664.0	1267.2
Permeation exit Cgi (ppb) at 0.075 lpm	3200.0	25600.0	12800.0	640.0
Certified generation rates, ng/min	380.9	3984.9	2181.6	107.5
Length (cm)	1.5	4.3	5.6	50F3***
Certification True Accuracy by NIST traceable standard	(±0.99%)	(±1.38%)	(±1.12%)	(±3.27%)
Certified exposure concentration, ng/L (µg/m³)	15.9	166.0	90.9	4.5
Certified exposure concentration, ppb	11.3	87.9	34.6	2.3
Generation method	Perm**	Perm	Perm	Wafer
Estimated useful life, months	12	10.5	12	9
* Total flow rate is 24 lpm.	1	1	1	1
**Perm: permeation tube				

Table 3-1 Generation of Pollutant Gases

Perm: permeation tube.

***Geometry: 50F3 (.05" thick * 3/16" dia F wafer).

 NO_2 Monitor (Table 3-2). Converter Models 400/401 (Figure 3-13) from 2B Technologies were used to measure the NO_2 concentration in the exposure chamber.

Category	Model 400 NO Monitor	Model 401 NO2 Converter			
Measurement Principle	Titration of NO with Ozone with Detection of Ozone Depletion by UV Absorption at 254 nm	Molybdenum Oxide at 325 degree Celsius			
Range N/A		0-2000ppb			
Accuracy	Higher of 3 ppbv or 3% of reading	N/A			
Time/Measurement	10 s (Data averaging options: 10 s, 1 min, 5 min, 1 hr)	10 s (Data averaging options: 10 s, 1 min, 5 min, 1 hr)			
Sample Flow Rate	1 L/min	2 L/min			



Figure 3-13 2B Tech. Models 400/401 NO_x Monitor

3.3.5. Gas Delivery System

In Figure 3-14, clear polycarbonate was used to fabricate the manifold box (which delivers mixed flow gas to the individual exposure chambers) in order to avoid the interaction between the manifold and the pollutant gases. There were two parts of the mixing chamber: the mixing part and the delivery part. All the moisture air and pollutants were injected into the mixing part, and then flowed through a small hole into the delivery part. The delivery part had six holes, each connected to an exposure chamber. The pressure drops between the hole and outlet were measured in order to make sure the uniformity of flow rate for each port. To check if the mixing was satisfactory, an ozone monitor was used to measure the ozone concentration at different chamber position. Results show that the differences of concentrations among the six exposure chambers used were within 2% (see Table 3-1).



Figure 3-14 Actual Mixing Chamber

3.3.6. Monitoring System

To monitor the system, a combined RH and temperature sensor (HC2S3 from Campbell Scientific) was used. It was placed inside the reference exposure chamber without exposing to the corrosive pollutants. The parameters of the sensor are shown in Table 3-1.

Meas	urement	Specifications					
	Sensor	PT100 RTD, IEC 751 1/3 Class B, with calibrated signal conditioning					
Temperature	Measurement Range	-50 to 100 °C (default -40 to 60 °C)					
Output Signal Range Accuracy at 23 °C Sensor Time Constan	Output Signal Range	0 to 1.0 V					
	Accuracy at 23 °C	± 0.1 °C with standard configuration settings					
	Sensor Time Constant	≤ 22 s (standard PE filter)					
	Sensor	ROTRONIC Hygromer® IN1					
Relative humidity	Measurement Range	0 to 100% non-condensing					
	Output Signal Range	0 to 1.0 Vdc					
	Accuracy at 23 °C	$\pm 0.8\%$ RH with standard configuration settings					
	Sensor Time Constant	\leq 22 s (standard PE filter)					

Table 3-1 Relative Humidity and Temperature Sensor

3.4. Test Specimens

3.4.1. Standard Coupon

The standard coupons (Figure 3-15), copper and silver, were supplied by Purifil. The size was 3.5 inch (length) by 0.5 inch (width) by 1/16 inch (thickness).



Figure 3-15 Standard Coupons for Copper and Silver

3.4.2. Printed Circuit Board (PCB)

This research focused on the corrosion of copper and silver metals used in the design and manufacturing of computer systems, primarily the assembly of components on printed circuit cards. A variety of components (processors, memory, optical devices, resistors, capacitors, etc.) are mounted to printed circuit cards (PCBs) using a variety of methods (surface mount, thru hole, etc.). Besides providing a structural platform for mounted components, the PCB's are primarily used to distribute power and signals to the array of components. This distribution is accomplished through

copper traces designed within and on the surface of the PCB. The power carrying traces are the focus here where the resulting current densities could result in a significant temperature rise that could influence the effect of corrosion.

In an effort to understand these effects, three different patterns of PCBs were designed to cover the range of current densities most experienced in the design of PCBs used in computer systems. Several circuit designers were contacted at IBM to aid in the determination of the range of current densities to test. They concluded that current densities from 20 to 140 A/mm² were appropriate according to their input. Three PCB test cards were designed based on the input to cover this range each designed for ease of testing with a constant current source of 1 A. The designs for a copper trace thickness of 35 µm are shown in Figure 3-17 below for varying trace lengths and widths that would provide temperature rises of 0.77°C, 7.5°C and 19°C. The widths of the traces for the three PCBs were 1.42 mm, 0.358 mm, and 0.203 mm, respectively (Figure 3-16). The PCBs were made by Advanced Circuit. For the PCB with traces of 1.42 mm width, a current of 0.33 A was tested resulting in a current density of 6.63 A/mm². In the MFG tests, the PCBs with the widest trace were used because it was easier to monitor and detect the corrosion results.



Figure 3-16 PCB Drawing (Left) and Actual PCB

4. Experimental Method, Procedure, and Design

4.1. Experimental Method

In a mixed flowing gas test, copper or silver coupons are exposed to the gas mixture for an extended period of time inside an exposure chamber maintained at a reference temperature and relative humidity (e.g., 21°C and 50% RH). The concentration levels of the pollutants in the gas flowing mixture inside the exposure chamber are typically elevated from those found in data center environment to accelerate the corrosion for testing. According to the ASTM Standard B827-05 Standard Practice for Conducting Mixed Flowing Gas (MFG) Environmental Tests, there are four major apparatus for a mixed flowing gas test: corrosion test chamber, gas supply system, chamber monitoring system, and chamber operating system. The detailed information about the apparatus used in the present study has been presented in Chapter 3. After the test specimens are exposed in the chamber for a pre-defined time, they are analyzed offline by coulometric reduction to determine the corrosion thickness, or by surface characterization methods such as SEM/EDS, AFM, and XPS to determine the composition and distribution of the corrosion products.

In this study, all of the standard test specimens/coupons were provided by Purifil. They were exposed in the exposure chambers at the BEESL in Syracuse University, and then shipped back to Purifil where they were analyzed by coulometric reduction. SEM/EDS and AFM analyses were performed at Syracuse University's Biomaterial Research Institute, and XPS analyses were performed at Intel's research lab and at Prof. Jeremy Gilbert's Lab at Clemson University. Prof. Jeremy Gilbert's Lab also supported one set of coupons and PCBs to do the SEM/EDS mapping analysis.

4.2. Experimental Procedure

4.2.1. Test Chamber Verification

According to the ASTM Standard B827-05 Standard Practice for Conducting Mixed Flowing Gas (MFG) Environmental Tests, when the exposure chamber has larger than 0.5 m along the direction of flow, the spatial uniformity of the corrosivity shall be measured. Our exposure chamber only had 0.016 m long on a side and was designed to provide uniform flow and exposure for the specimen surfaces. To verify the uniformity of flow rate and pollutants' concentrations, we performed two measurements: pressure drop across each exposure chamber (which would ensure the same flow rate through each chamber) and O_3 concentrations in different exposure chambers that were connected to different ports of the same mixing chamber (see Chapter 3.3.5).

A manometer was used to measure the pressure drop across each chamber. The manometer had two tubes, which were connected to the inlet and the outlet of exposure chamber, respectively, to measure the pressure drop across each exposure chamber. The pressure drop is the function of flow density, k factor and air velocity, ΔP – pressure drop ($\Delta P = k \times (0.5 \times d \times v^2)$), k- factor (a factor is related with the frictional losses, the losses from expansion and contraction and inlet losses, which will impact the pressure drop), d – typical air density, and v – air velocity). The data were used to calculate the friction coefficient of each chamber. The friction coefficients were then used to calculate the flow rate for each exposure chamber when the total flow rate was 24 lpm. As shown in Table 4-1, the standard deviation of flow rates among the 6 exposure chambers was 0.2 lpm at 24 lpm total flow rate — i.e., 5% of the average flow rate per chamber (4 lpm), which was considered acceptable. The average air velocity in the chamber was 19.44 ft/min, which was much larger than the required 5 fpm, beyond which the effect of velocity on the corrosion is negligible (Abbott 1988).

No. chamber	Pressure Drop (Pa)	k Factor	Q (lpm)	Velocity(fpm)
1	8.75	83.79	3.73	18.12
2	8.3	79.48	3.83	18.6
3	7.9	75.65	3.92	19.07
4	6.85	65.59	4.21	20.48
5	6.85	65.59	4.21	20.48
6	7.25	69.42	4.1	19.9
Standard Deviation		0.2	0.996	

Table 4-1 Measured Pressure Drops, Flow Rates and Air Velocities for the Exposure Chambers

An ozone monitor was used to measure the ozone concentration in different exposure chambers. As shown in Table 4-2, the ozone concentration among the six chambers had a standard deviation of 1 ppb.

No. Chamber	Ozone Concentration (ppb)					
1	50					
2	51.96					
3	52					
4	53.1					
5	51.96					
6	51.66					
Average (ppb)	51.78					
Standard Deviation (ppb)	1					

Table 4-2 Uniformity of Pollutants' Concentration

4.2.2. Test Preparation

Copper and silver coupons were taken out from the packages sent by Purifil (Figure 3-15) and then were hung in parallel on a threaded rod, keeping the same distance between the coupons (see Figure 3-5). They were then inserted into the exposure chambers from the top. For the printed circuit cards (Figure 3-17), they were first rinsed in acetone for 1 minute and flushed with dry air before they were inserted into the exposure chambers.

To prepare for pollutant generation, the permeation tubes for NO₂, SO₂, H₂S, and Cl₂ were inserted into the temperature-controlled tube of the Dynacalibrator and the channel's cap (Figure 3-2) was closed tightly. The mass flow controller for ozone generation was set at 2 lpm. The thermal environmental conditions in the exposure chamber including temperature and relative humidity were kept within $\pm 1^{\circ}$ C and $\pm 3\%$ STD, respectively of the set points in average over the test period. The gas concentrations were kept within $\pm 15\%$ or ± 3 ppb of the test concentration levels.

4.2.3. Test Procedure

For each test, the test system was first turned on to achieve the desired airflow rates, temperature, and relative humidity in the exposure chamber. The permeation tubes were then placed in the dynacalibrator for the generation of SO_2 , NO_2 , Cl_2 , and H_2S , and the ozone generator was set to achieve the desired concentration. After the concentrations reached stable levels, the pre-assembled sets of copper and copper coupons were placed inside the exposure chambers, and the time was recorded as time zero for the exposure. The coupons were removed from the exposure chambers when the pre-defined exposure time was reached. They were then photographed,

packaged, and shipped to the analytical lab for coulometric analysis or saved for SEM/EDS, AFM or XPS analyses. Detailed step-by-step procedure is described in Appendix I.

4.3. Experimental Design: Test Conditions

Eight different combinations of pollutants were tested to investigate the effects of pollutant gases on corrosion:

- I. MFG1: NO₂, SO₂, O₃, which are most prevalent in atmospheric pollution; Four combinations were tested:
 - 1) O_3 , to examine if O_3 alone would cause any corrosion.
 - 2) O_3+NO_2 , to examine the synergistic effect of O_3 and NO_2 .
 - 3) O_3+SO_2 , to examine the synergistic effect of O_3 and SO_2 .
 - NO₂+SO₂+O₃, which are most prevalent in atmospheric pollution and in data center environment.
- II. MFG2: NO₂+SO₂+O₃+H₂S, to examine the synergistic effect between NO₂+SO₂+O₃ and H₂S.
- III. MFG3: NO₂+SO₂+O₃+Cl₂, to examine the synergistic effect between NO₂+SO₂+O₃ and Cl₂.
- IV. MFG4: NO₂+SO₂+O₃+ H₂S+Cl₂, which represent the most pollutant case in which all five pollutants are present (i.e., the "worst realistic mixture and concentrations).
- V. MFG5: $NO_2+SO_2+H_2S+Cl_2$, to examine the corrosion effects when O_3 is not present.

Concentrations of the pollutants were pre-selected based on the comprehensive literature review and analysis, which represent "realistic indoor worst case" conditions (Table 2-7) that could be experienced by data centers based on the literature review (see Chapter 2):

Table 4-3 "Realistic" Indoor Worst-case Concentration Levels

Gas	H_2S	NO ₂	SO_2	Cl ₂	O ₃
Concentration (ppb)	10	80	40	2	60

Table 4-4 Summary for Test Conditions

Test Set #	T (°C)	RH (%)	Pollutant	Test Time (day)
1 (Reference)	21	50	MFG1 -1), 2), 3), 4)	6, 6, 6, 6
			MFG2, 3, 4, 5	6, 6, 30, 6
2 (A1)	21	70	MFG1 - 3)	6
			MFG3,4,5	6, 12, 6
3 (A1)	28	50	MFG1 - 1), 2), 3), 4)	6, 6, 6, 6
4 (A1)	21	80	MFG1 - 1), 2), 3), 4)	6, 6, 6, 6
5 (Duplicated)	21	50	NO ₂ +O ₃	6
6(A1)	21	80	MFG2,3,4	6, 6, 6, 6
7 (A1)	28	50	MFG2,3,4	6, 6, 6, 6
8 (RH fluctuation)	21	50	MFG4	5
9 (RH fluctuation)	21	80	MFG1 – 4)	5
10	21	50	NO ₂	6
11	28->21	50	MFG4	6+6



Figure 4-1 Test Conditions (ASHRAE,2015)

Table 4-4 summarizes the temperature, relative humidity, combinations of pollutant gases, and test period used the experiments conducted in the present study. Rational for the selection of the test conditions are given below:

• Test Set 1: 21°C and 50% RH is the reference condition, which is also within the recommended thermal envelope for data center operation (Figure 4-1). One of the important objectives of the present study was to determine under which condition we could expand the recommended thermal envelope without causing additional corrosion. We chose the recommended thermal envelope condition to be the reference and investigated if deviations from this condition would cause additional reliability issues. We first performed a 30-day test for five-compound MFG (i.e., pollutant combinations MFG4) under the reference condition, and then changed to 6-day tests because sufficient corrosion could already be observed after 6 days exposure. This also allowed more combinations of pollutant species to be performed.

- Test Set 2: It is a condition with a higher relative humidity to investigate the effects of RH on the corrosion levels for the selected combinations of pollutant species. It is within the ASHRAE's A1 thermal envelope for ITE (Figure 4-1). The 12-day test was for the fivecompound exposure (MFG4), and the 6-day tests were for the remaining combinations of pollutant species.
- Test Set 3: It is a condition with a higher temperature (28°C) while keeping the 50% RH unchanged from the reference case. We focused on the three most pervasive pollutants, O₃, SO₂, and NO₂.
- Test Set 4: It is a condition in which we further raised the relative humidity to 80% RH at 21°C, the maximum level for ASHRAE's A1 thermal envelope for ITE.
- Test Set 5: It is a duplicate test for the reference condition to confirm the synergistic effects between NO₂ and O₃.
- Test Set 6: It is a condition with high temperature and high relative humidity, representing the worst thermal condition that may be experienced by ITE. Tests were performed for four and five pollutant mixture only to focus on cases where corrosion is more significant.
- Test Set 7: It is a condition with a higher temperature while keeping the same relative humidity as the reference case, locating the thermal condition on the upper boundary of ASHRAE's A1 envelope.
- Test Set 8: To investigate the effect of RH fluctuation under the reference RH condition (50%) at 21°C.
- Test Set 9: To investigate the effect of RH fluctuation under the high RH condition (80%) at 21°C.

- Test Set 10: A test for a single pollutant, NO₂, to obtain baseline data for analyzing the possible synergistic effects of NO₂ with other compounds.
- Test Set 11: A duplicated test in order to confirm the temperature effect on corrosion and if pollutants' concentrations are consistent with the previous tests.

4.4. Corrosion Detection and Analysis

4.4.1. Visual Inspection, Image Analysis, and Color Indexing

After exposing the coupons under various mixed gas flows, photos were taken to show the corrosion color change. A photo box was designed for uniform and consistent illumination.

In order to run photo analysis, the lighting conditions to take the picture needed to be uniform. A photo light box was built for this purpose. It was made from a cardboard box, diffusion fabric, a white poster, a clip lamp, and two 100 W fluorescent light bulbs (Figures 4-2 and 4-3). The light box was created by cutting holes on the side of the cardboard box and covering them with the



Figure 4-3 Photo Light Box - Front



Figure 4-2 Photo Light Box - Side

diffusion fabric. The inside of the box was covered with white poster paper and a hole was cut on the top of the box to create an opening to take the pictures. Two lamps were placed against the diffusion fabric to light up the box. In addition to setting up the box, the camera needed to be white balanced, which was achieved by using gray cards.

A MATLAB code was developed to calculate the intensity value of red, green, and blue (RGB value) for each coupon tested. A higher RGB difference was found to correspond to a more severe corrosion for copper and silver, although the RGB difference values could not distinguish corrosion thickness below 500 Angstroms (Figure 4-4).



Figure 4-4 Correlations Between the Corrosion Thickness and Color Index (RGB difference is equal to RGB of the exposed coupon – RGB of the clean coupon. It represents the change of RGB due to corrosion)

4.4.2. Coulometric Reduction

Coulometric reduction is an electrochemical-based technique. The technique is based on ASTM Standard B825-13, Standard Test Method for Coulometric Reduction of Surface Films on Metallic

Test Samples. 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. The quantity of electricity is shown by monitoring the voltage change as the corrosion products are dissolved into the electrolyte at some constant current. It is a common technique to estimate the corrosion rate of copper and silver. However, it cannot be applied to in-situ studies, and the samples analyzed are destroyed in the process, and cannot be re-analyzed or placed back to the environment for exposure to continue the corrosion process. All the standard copper and silver coupons (Figure 3-15) were analyzed by Purifil, in which they provided the 30 days normalization data for the corrosion thicknesses. Using the formula in Equation (4-1) used for the copper corrosion Appendix C on Page 25 from the ISA standard, we calculated the "actual" amount of corrosion during the exposure period as follows:

For copper corrosion,

$$x_1 = x(t_1/t')^A, (4-1)$$

where:

 x_1 is the equivalent film thickness after 30 days;

x is the measured film thickness after time t';

 t_1 is thirty days;

t' is the actual test time (days);

A is equal to 0.3 for G1, 0.5 for G2, and 1 for G3 and GX (according to classification of reactive environments).

The relationship between the corrosion thickness and exposure time is considered to be linear for silver corrosion.

Severity level	G1 Mild	G2 Moderate	G3 Harsh	GX Severe
Copper reactivity level (in angstroms)*	< 300	< 1000	< 2000	≥2000
Silver reactivity level (in angstroms)*	< 200	< 1000	< 2000	≥2000

An example output of coulometric output is given in Table 4-6. For each row, the first column is to describe the exposure condition for coupons. The second column is the coupon number on the panel where the copper and silver were stored. The third column is the number of exposure chamber to show the location where the coupons were exposed. The fourth column is to show the exposure time of coupons in days. The fifth column is the classification of copper corrosion according to the above equation and Table 4-5. The sixth column is the copper corrosion thickness after exposing the days in the fourth column. The seventh to the tenth column is the copper corrosion thickness after normalizing 30 days exposure for each compound. The eleventh to the final column is to repeat the content from fifth to tenth but for silver.

Exposure	CCC Panel	Chamber	Days in	Copper	Copper	Copper	Cu2S	Cu2O	Cu- Unk	Silver	Silver	Silver	AgCl	Ag2S	Ag- Unk
condition	No.	No.	Servic e	Class	Actual (calc.)	30-day	Ang.	Ang,	Ang.	Class	Actual (calc.)	30- day	Ang.	Ang.	Ang
	113223	4	3	1	1560.5	15605	0	5489	1011 6	1	1640.1	16401	677	12218	3506
	113151	4	3	1	263.2	2632	0	1832	800	1	1245.9	12459	677	11782	0
	113190	2	6	1	1307.6	6538	0	2745	3793	1	2704.8	13524	677	11345	1502
	113193	2	6	1	1703.2	8516	0	3964	4552	1	2698.6	13493	677	11564	1252
	113225	3	12	1	4320	10800	0	2707	8093	1	5654.4	14136	761	12436	939
	113187	3	12	1	3283.2	8208	0	2897	5311	1	5684.8	14212	677	11782	1753
21C 50%RH	113124	4	20	1	4912	7368	0	1830	5538	1	7738.66 667	11608	609	10473	526
five pollutants	113142	4	20	1	5058.66 67	7588	0	1670	5918	1	8037.33 333	12056	609	10996	451
	113136	2	25	1	7040	8448	0	1043	7405	1	9777.5	11733	650	10813	270
	113203	2	25	1	6965	8358	0	1317	7041	1	9822.5	11787	893	10473	421
	113139	5	30	1	6427	6427	0	610	5817	1	13466	13466	711	12480	275
	113211	5	30	1	5790	5790	0	732	5058	1	12791	12791	745	11695	351
	113123	7(referenc e)	30	0.3	305	305	0	305	0	0.5	262	262	0	262	0
	113171	7(referenc e)	30	0.3	290	290	0	290	0	0.5	218	218	0	218	0

Table 4-6 Example of Output of Coulometric Reduction (See Appendix II for all the data)

All test data are provided in Appendix II.

4.4.3. Scanning Electron Microscopy and Energy Dispersive Spectrometry (SEM/EDS)

A Hitachi SN5700, Oxford Instruments X-ray Energy Dispersive analyzer was used to perform the scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS) in Figures 4-5 and 4-6. Both secondary and backscattered electron imaging modes were used to characterize the surfaces. Because the atomic number can be inferred from the differences in backscattered emission efficiency (higher Z results in brighter signal), backscattered electron images provide some information related to the chemistry. This allowed the identification of corrosive materials covered regions of the samples. Both energy dispersive x-ray spectra and elemental maps were generated and correlated to SEM images (Chapter 5). The highest magnification is of the order of 10^5 , corresponding to a ~ 5nm lateral resolution. As an example, Figure 4-5 shows that the micrographs of the copper bottom region at high magnification (15kV). Figure 4-6 and Figure 4-7 show the spectra information for spectrum 1.



Figure 4-5 a) Secondary and b) Backscattered Electron Micrographs of the Copper Bottom Region at high Magnification (15kV), which was exposed under 21°C, 80%RH and MFG+Cl₂.

In Figure 4-5, a) represent the geometry of the surface and b) represent the composition on the surface. The dark lines represent the oxides products. Most of the shining parts are copper.



Spectrum 1							
Cmpd	wt%						
S	6.325						
Cu	93.675						

Figure 4-6 Spectra Locations in Backscattered Electron Micrograph

EDS detected the spot that is marked in Figure 4-6 and produced the spectrum results. Spectrum 1 shows that the grey dark location consists of sulfide and copper elements. The table of spectrum 1 came from Figure 4-7 which presents the element detection results.



Figure 4-7 Spectra Profile for Spectrum shown in Figure 4-6

4.4.4. Atomic Force Microscopy (AFM)

In AFM, the forces between a cantilever of surface probe and the surface are used to detect the morphology of a surface. This technique was used to monitor the deflection of a surface as a function of the corroded surface, with a resolution in the order of a few tenths of a nanometer. It also helped us to capture the roughness differences under various exposure conditions for copper and silver coupons. As an example, Figures 4-8 and 4-9 show the height (left) and deflection (right) of copper and silver surface. It can help us to understand how the coupon surface is covered by corrosion products.



Figure 4-8 Height and Deflection for Copper (Exposed under 21°C, 50% RH and NO₂+SO₂+O₃)

In Figure 4-8, the left figure shows the height distribution of the copper surface, where lighter colors represent higher surface locations. The right figure shows the deflection of the copper surface. The convex dots represent the corrosion products or/and particle deposition on the surface. Compared to the copper surface, the silver surface is smoother and has smaller dots in Figure 4-9.



Figure 4-9 Height and Deflection for Silver (Exposed under 21°C, 50% RH and NO₂+SO₂+O₃)

4.4.5. X-ray Photoelectron Spectroscopy (XPS)

A Quantum 2000 Scanning ESCA (Electron Spectroscopy for Chemical Analysis) microscopy (Physical Electronics, US) system was used to obtain XPS spectra. It used Al radiation ka=1486.6 eV with passing energy of 117.40 eV. The takeoff angle between the sample surface and analyzer was 45°. Spectral Acquisition mode and Sputter Depth Profile mode were conducted on samples at different positions. Using spectral acquisition analyzed chemical states of different elements (Cu/Ag C S O Cl N). Depth profile performed the element spectral/element distribution at different depths from surface. It can give some useful information about the corrosion product distribution along the depth of a corroded coupon and in identifying the corrosion compounds. As an example, Figure 4-10 shows Cu 2p spectrum including Cu, Cu₂O, CuO, and Cu (OH)₂. The mint line represents Cu, the green represents Cu(OH)₂, the blue line represents CuO₂, the purple line represents CuO, while the red line represents the sum of these four chemical products.

In Figure 4-10, it also shows the ratio of each corrosion products, which helps us to understand corrosion mechanism.



Figure 4-10 Cu 2p XPS Spectrum

5. Experimental Results

5.1. Corrosion Thickness and Corrosion Products (Coulometric Reduction)

Coulometric reduction analysis gave the corrosion thickness for copper and silver coupons. All corrosion thickness results accounted for the background corrosion thickness measured from the reference coupons for a given set of tests, which ranged from 80 to 2000 Angstroms (See Appendix II, which includes the reference coupon corrosion thickness in the chamber No. 7 for each test). Based on 196 sets of duplicate sample analyses, the mean standard deviation is 270.85 Angstroms for copper and 103.18 Angstroms for silver. The median of relative standard deviation (ratio of the standard deviation to mean standard deviation) is 48.15% for copper and 80.66% for silver.

5.1.1. Corrosion Development over Time

As shown in Figure 5-1, the measured corrosion thickness for copper and silver increased with the exposure time as expected. The increase for copper over the exposure time was non-linear but followed a logarithmic relationship approximately within the range of 3 to 30 days of exposure. The increase in corrosion thickness for silver over time was linear.



Figure 5-1 Corrosion Development over Time for Copper and Silver (21°C 50%RH NO₂+SO₂+O₃+H₂S+Cl₂)

Results from the coulometric reduction also show that the major corrosion products after the 30day exposure included Cu₂O (11%), Cu-unknown (89%) – likely be Cu₂S, CuSO₄, and CuCl₂. Increasing the exposure time results in the Cu₂O and Cu-unknown corrosion thicknesses increasing at first, then after 12 days the rate of growth of the corrosion thickness begins to diminish. The thickness (or amount) of these corrosion products varied with the exposure time (Figure 5-2), suggesting complicated corrosion mechanisms possibly involving multi-synergistic effects among the pollutants and moisture, which will be further discussed later.

For silver, the significant corrosion product is Ag_2S in Figure 5-3 during the exposure time. The ratio of AgCl has slightly grown over time. But the ratio of Ag-unknown (likely include Ag_2O) decreases and the ratio of Ag_2S increases.

For copper and silver, it shows how the oxidized products are consumed with the exposure time. A possible reason is that the pollutants NO_2 , SO_2 , O_3 , Cl_2 , and H_2S destroy the oxidized layer which can protect the coupons from corrosion so that they can contact the pure subbase of metal.



Figure 5-2 Corrosion Development over Time – Ratio of Corrosion Products (Cu₂O and unknown products) for Copper



Figure 5-3 Corrosion Development over Time – Ratio of Corrosion Products (AgCl, Ag₂S, and unknown products) for Silver

5.1.2. Effects of Pollutant Mixture

Figure 5-4 and 5-5 summarize the results of the measured corrosion thickness after 6 days exposure for all combinations of pollutant mixtures, temperature, and relative humidity conditions tested, with subtraction of the reference corrosion thickness.



Figure 5-4 Effects of Pollutants Mixture – Copper Corrosion Results after Exposure 6 Days (Coulometric Reduction



(Coulometric Reduction)

For the reference temperature and RH condition (21°C and 50% RH), significant copper corrosion occurred only for the four-compound mixtures of NO₂+SO₂+O₃+Cl₂ and NO₂+SO₂+Cl₂+H₂S, and for the five-compound mixture of NO₂+SO₂+O₃+Cl₂+H₂S (Figure 5-4). These results suggest that Cl_2 had the most corrosive effect on copper. Without Cl_2 the corrosion thicknesses were significantly less. This was the case even when the relative humidity was increased to 70% RH. However, for silver, significant corrosion occurred only when H₂S was in the pollutant mixture (Figure 5-5). Cl_2 did not show the same effect for silver as for copper.

The dominating effect of H_2S for silver corrosion was evident from the corrosion products (Ag₂S is the dominating product) identified from the coulometric analysis results (Figure 5-6). But when using the coulometric reduction for evaluating copper, it is difficult to detect CuCl₂ as the main corrosion product, because CuCl₂ is soluble in the water and coulometric reduction process detects corrosion products which are not soluble in the water. Therefore, Figure 5-7 cannot determine the dominating effect of Cl₂ for the corrosion of copper.




=21C 50%RH =21C 70%RH =21C 80%RH =28C 50%RH

Corrosion Product to Different Pollutant Combinations

21C 50%RH

Cu20 Cu-unlenown N02+S02+CI2+H2S

Cu2S

Cu20 Cu-unknown MFG+Cl2+H2S

Cu2S

Cu20 Cu-unknown

Cu2S

Cu-unknown

Cu20 MFG+Cl2

Cu2S

Cu-unknown

Cu20 MFG

Cu-unknown

Cu20 S02+03

Cu2S

Cu-unknown

Cu20 N02+03

Cu2S

Cu-unknown

Cu20

Cu2S

۱ Cu2S

MFG+H2S

5.1.3. Effects of Relative Humidity

For copper, increasing the relative humidity from 50% RH to 70% RH further increased the corrosion thickness for the three Cl₂-containing mixture conditions mentioned above. Further increase of the relative humidity to 80% RH not only increased corrosion thickness for these three mixture conditions, but also resulted in significant corrosion for all other test mixtures (Figure 5-8). This suggests that a critical relative humidity exists between 70% and 80% RH, above which corrosion would significantly increase regardless of the pollutant mixture conditions. Hence, even for those pollutant mixtures tested without Cl₂ the relative humidity above 70% RH should not be recommended for data center environment.





For silver, however, increasing the relative humidity did not cause a significant increase in the corrosion thickness for two H₂S-containing mixtures mentioned above (Figure 5-9), but these two H₂S-containing mixtures still caused significant corrosions, which are higher than the limit of 200 Å/month. For the five-compound mixture, increasing the relative humidity from 50% to 70%RH and even to 80%RH resulted in a reduction in the corrosion thickness (Figure 5-9), though the corrosion thickness was still out of the silver corrosion limit of 200 Å/month. While the mechanism for this phenomenon is not clear, it is possible that the corrosion product at high 80% RH covered the coupon surface quickly and slowed down further corrosion.





Figure 5-8 shows that, for copper, increasing the relative humidity increased the corrosion thickness of identified corrosion products for the three and four pollutant mixture combinations. For silver, Figure 5-9 shows that relative humidity did not have much influence on the corrosion thickness except for the five-compound mixture.









Figure 5-9 Corrosion Thickness for Each Product - Silver

21C 50%RH 21C 70%RH 21C 80%RH 28C 50%RH

Corrosion Product to Different Pollutant Combinations

Figure 5-8 Corrosion Thickness for Each Product - Copper

Figure 5-10 shows that increasing relative humidity decreases the ratio of the corrosion product Cu_2O . More moisture doesn't cause thicker copper oxide.



Figure 5-10 Effect of Pollutant Mixture - Ratio of the Corrosion Product Cu₂O - Copper

For silver, Ag₂S increases when relative humidity increases from 50% to 80% RH at 21°C in Figure

5-11. It shows that the higher relative humidity causes the formation of silver sulfide.



Figure 5-11 Effect of Pollutant Mixture - Ratio of the Corrosion Product Ag₂S - Silver

5.1.4. Effects of Temperature

For copper, increasing the temperature from 21°C to 28°C while keeping the relative humidity at the reference condition (50% RH) dramatically reduced the corrosion thickness for all mixture conditions tested (Figure 5-12). This was unexpected, but a repeat test confirmed the observation. According to the book (Christofer Leygraf, 2000), increasing the temperature not only reduces the time of wetting on the surface, but also decreases the solubility of the pollutant gases, including oxygen. It was likely that at a higher temperature fewer pollutant (especially Cl₂) could be adsorbed or absorbed on the test coupon's surface to cause corrosion.



Figure 5-12 Effects of Temperature – Copper Corrosion Results after Exposure 6 Days (Coulometric Reduction)

However, for silver, a significant corrosion still occurred at 28°C, though a reduction can also be observed when the temperature was increased from 21°C to 28°C at the same 50% RH condition (Figure 5-13). Further analysis is needed to understand the mechanisms.



Figure 5-13 Effects of Temperature – Silver Corrosion Results after Exposure 6 Days (Coulometric Reduction)

From Figures 5-14 and 5-15 the thicknesses of each compound obviously decreased when the temperature increased for copper whereas it didn't significantly affect the corrosion thickness for silver. Increasing the temperature decreased the ratio of Cu_2O for copper.



Figure 5-14 Effect of Temperature - Ratio of the Corrosion Product $Cu_2O - Copper$ For silver, when temperature increased from 21°C to 28°C at 50%RH, the ratio of Ag₂S decreased except for NO₂+SO₂+O₃ in Figure 5-15.



Figure 5-15 Effect of Temperature - Ration of the Corrosion Product Ag₂S - Silver

5.2. Color Index

After the coupons were exposed under different conditions they were photographed by a digital camera and the images were analyzed to determine the RGB (red, green, black color index) values for quantifying the changes of color index due to the corrosion. In the coupon pictures shown below, the red arrows below each picture show the airflow direction.

5.2.1. Corrosion Development over Time



Figure 5-16 Change of Color for Copper and Silver after Exposure 30 Days under 21°C 50%RH $NO_2+SO_2+O_3+Cl_2+H_2S$

Figure 5-16 shows that with increasing the exposure time to pollutants, the copper surface became darker and darker while the silver surface became more colorful. The corresponding RGB values decreased over time (Figure 5-17). There was a very obvious color gradient on the silver surface, which was caused by the corrosion gradient along the MFG flow streams. Both copper and silver

had a darker color at the bottom of the coupons (upstream) than the middle or top of coupons (downstream). This was likely due to the reduction of the pollutant concentration downstream as some of the pollutants have been consumed due to the corrosion at the upstream locations, and the development of the boundary layer over the surfaces.



Figure 5-17 Change of Color Index over Exposure Time for Copper and Silver under 21°C 50%RH NO₂+SO₂+O₃+Cl₂+H₂S

5.2.2. Effects of Pollutant Mixture

Figure 5-18 through Figure 5-20 show the images and the RGB color index of the test coupons after exposure to different pollutant combinations under 21°C 50% RH, 21°C 80% RH, and 28°C 50% RH. In various combinations of three pollutants (O₃, NO₂, and SO₂), Ozone and NO₂ caused more corrosion than SO₂ with ozone. According to the RGB color index values in Figure 5-21 and Figure 5-22, Cl₂ caused more corrosion to copper than to silver, but H₂S caused more corrosion to silver than to copper.



(g) NO₂+SO₂+H₂S+Cl₂ 6 Days

Figure 5-18 Images for Copper and Silver Coupons after Exposure 6 Days under 21°C 50% RH (MFG: NO₂+SO₂+O₃)



(g) Reference 6 Days

Figure 5-19 Images for Copper and Silver Coupons after Exposure 6 Days under 21°C 80% RH (MFG: NO₂+SO₂+O₃)



(g) Reference 6 Days





Figure 5-21 Effects of Pollutants Mixture – Copper RGB Values after Exposure 6 Days (Color Index)



Figure 5-22 Effects of Pollutants Mixture – Silver RGB Values after Exposure 6 Days (Color Index)

5.2.3. Effects of Temperature

Figure 5-20 compares the images of coupons exposed to 21°C and 28°C, respectively, under the same combinations of mixing flow gases and relative humidity (50% RH).



Figure 5-23 Images of Copper and Silver Coupons after Exposure 6 Days under Different Temperatures

 $(MFG: NO_2 + SO_2 + O_3)$

Most of the coupons exposed to 28°C 50% RH appeared to have slightly darker colors. The RGB color index also exhibits slightly higher values (darker) at 21°C than at 28°C (Figure 5-24 and 5-25). However, these differences do not imply more corrosion at 28°C. In fact, the corrosion was much less at 28°C than at 21°C as shown by the data from the coulometric analysis. This means that when the difference in RGB values is small, the color indexing approach does not necessarily reflect the differences in the corrosion severity (Figure 5-26).



Figure 5-24 Effects of Temperature – Copper RGB Values after Exposure 6 Days (Color Index)



Figure 5-25 Effects of Temperature – Silver RGB Values after Exposure 6 Days (Color Index)



Figure 5-26 Regression of Color Index to Corrosion Thickness (RGB in this figure is the RGB difference between the clean coupon and the exposed sample).

A lower RGB difference corresponds to a lower corrosion thickness although it cannot distinguish corrosions below 500 Angstroms and 400 Angstroms for copper and silver, respectively. The RGB color index method should therefore only be used as an initial screening approach to detect possible corrosion.

5.2.4. Effects of Relative Humidity

Figure 5-27 compares the images of coupons exposed to 50% and 80% relative humidity, respectively under the same temperature (21°C).



Figure 5-27 Images of Copper and Silver Coupons after Exposure 6 Days at 50% RH (left) and

80% RH (right) (MFG: NO₂+SO₂+O₃)

With the exception of the exposure to " $NO_2+SO_2+O_3+H_2S$ ", the 80% RH exposure leads to darker images (lower RGB index values) due to much higher levels of corrosion than the 50% RH exposure (Figure 5-28 and 5-29), as were confirmed by the data from the coulometric analyses (see section 5.1).



■ 21°C 50%RH ■ 21°C 70%RH ■ 21°C 80%RH

Figure 5-28 Effects of Relative Humidity – Copper RGB Values after Exposure 6 Days



Figure 5-29 Effects of Relative Humidity -- Silver RGB Values after Exposure 6 Days (Color Index)

5.3.Surface Composition (SEM/EDS)

SEM and EDS are used to identify the morphology and chemistry of the surface after being exposed to pollutants. Selected coupons were analyzed with SEM and EDS at Syracuse University after 6 days of exposure. Additional coupons were analyzed by Prof. Gilbert at Clemson University using the same type of tools. They were exposed to $NO_2+SO_2+O_3+H_2S+Cl_2$ at 21°C and 50% RH for 25 days. Samples were imaged by EDS to get the distribution of elements on the coupon surfaces.



Figure 5-30 Copper a) Secondary (Left) and b) Backscattered (Right) Electron Micrographs of the Top Region at High Magnification (8.5kX)

Figure 5-30 shows that there are oxide needles and oxide patches irregularly distributed over the surface. The oxide regions appear darker gray (in b) with the brighter contrast metal situated underneath.



Figure 5-31 Copper Backscattered Images from which the Following EDS Analysis was Performed (21°C 50% RH NO₂+SO₂+O₃+H₂S+Cl₂ Exposure 25 Days)



Figure 5-32 Copper EDS Map of Figure 5-19 (21°C 50% RH NO₂+SO₂+O₃+H₂S+Cl₂ Exposure 25 Days)

In Figure 5-31, there is a small Ag particle (bright) and Si particle (dark) present along with oxide patches. This Ag on copper coupon is likely from a contamination particle. The EDS map in Figure 5-32 shows heterogeneous distribution of the elements present. The green regions (oxide) are heterogeneously distributed on the image. Cl, S, and C were identified as well. This heterogeneous distribution suggests that the corrosions initiated and developed in certain local spots that had more favorable conditions for the development while the other locations remained uncorroded. This is important since it suggests that the traditional layered model (Multi-regime perspective on the atmospheric corrosion) may not be applied, or at least cannot be applied uniformly to all surface areas. A new approach that accounts for the heterogeneous feature is needed. Note that Cl is clearly detected (yellow color), confirming the significant role Cl_2 played in the corrosion, which was not detectable by the coulometric method.



Figure 5-33 Copper Backscattered Images from which the Following EDS Analysis was Performed (21°C 50% RH NO₂+SO₂+O₃+H₂S+Cl₂ Exposure 25 Days)



Figure 5-34 Copper EDS Map of Figure 5-30 (21°C 50% RH NO₂+SO₂+O₃+H₂S+Cl₂ Exposure 25 Days)

Figure 5-33 and 5-35 show that the grey area is oxide of copper and the needle dots maybe C, Cl, S, and others. These kinds of needle dots also can be detected by AFM. In AFM, they exist as convex dots on the surface (Figure 5-42, see 5.4).

5.3.1. Effects of Pollutants Mixture

Under 28°C and 50% RH, when adding H_2S and Cl_2 to $NO_2+SO_2+O_3$, there were more sparkling dots on the copper and no much difference for silver (Figure 5-35 (a) vs. (c) and Figure 5-36 (a) vs. (c)). It is also consistent with the coulometric analysis for both copper and silver.



Figure 5-35 Effects of Pollutants Mixture - SEM/EDS (Copper, MFG: NO₂+SO₂+O₃)



Figure 5-36 Effects of Pollutants Mixture - SEM/EDS (Silver, MFG: NO₂+SO₂+O₃)

5.3.2. Effects of Temperature

Comparing Figure 5-37 (a) to Figure 5-37 (c) for 28°C and 50%RH MFG: NO₂+SO₂+O₃, there is a less smooth surface than for 21°C 50% RH and more shiny spots including Cu on the surface.



Figure 5-37 Effects of Temperature - SEM/EDS (Copper, MFG: NO₂+SO₂+O₃)

In Figure 5-38 (a) and (c), for silver, an increase in temperature doesn't seem to have much influence on the distributions of dots and needles on the surface. This is a similar trend as the coulometric analysis for silver but not for copper.



Figure 5-38 Effects of Temperature - SEM/EDS (Silver, MFG: NO₂+SO₂+O₃)

5.3.3. Effects of Relative Humidity

For copper, under $NO_2+SO_2+O_3$ after increasing relative humidity from 50% to 80% at the same temperature 21°C, there are some different compositions on the surface which look like a flower. According to EDS analysis (this method shows the composition of corrosion product in grey/black), most of the composition on the surface in Figure 5-39 (c) are copper and copper sulfide. The dark area has more sulfide than the light area.



Figure 5-39 Effects of Relative Humidity - SEM/EDS (Copper, MFG: NO₂+SO₂+O₃)

For silver and for NO₂+SO₂+O₃ with 21°C and 50% RH the coupon has a similar chemical distribution as with 21°C and 80% RH, except that the coupon under 80% RH has larger dots (Figure 5-40 (a) and (c)). This phenomenon is consistent with the coulometric analysis results. The changes in the silver sample are far less dramatic than the copper sample, suggesting a much less impact of RH on the silver corrosion for SO₂+NO₂+O₃ mixture.



(c) 21°C 80%RH MFG 6 Days -Ag (SEI) (d) 21°C 80%RH MFG 6 Days -Ag (BEI) Figure 5-40 Effects of Relative Humidity - SEM/EDS (Silver, MFG: NO₂+SO₂+O₃)

5.4. Surface Geometry (AFM)

Atomic Force Microscopy (AFM) was performed to reveal the micro/nano scale ($5nm \times 5nm$, scanning sample area) geometric characteristics of the corrosion surfaces including the size of corrosion products and surface roughness.

5.4.1. Effects of Pollutants Mixture

Compared to $O_3+SO_2+NO_2$ exposure, $NO_2+SO_2+O_3+H_2S+Cl_2$ caused much larger corrosion product dots to both copper and silver [comparing (a) vs. (c) for copper vs. (d) for silver in Figure 5-41]. Figure 5-42 shows the roughness for five compounds was larger than for three compounds for silver, but not for copper.



Figure 5-41 Effects of Pollutants Mixture – Surface Geometry for Copper and Silver Coupons after Exposure 6 Days (AFM)



Figure 5-42 Effects of Pollutants Mixture – Surface Roughness for Copper and Silver Coupons after Exposure 6 Days under 28°C and 50% RH (AFM)

5.4.2. Effects of Temperature

When the temperature was increased from 21°C to 28°C, there was still some convex dots, but they did not cover the copper surface uniformly [Figure 5-43(c)]. However, it was not obvious that increasing the temperature changed the roughness of the silver surface [Figure 5-43(d) and 5-45]. These results confirmed that at the microscale increasing temperature to 28°C indeed reduced the corrosion for copper as measured by the coulometric method.


(c)28°C 50%RH MFG 6 Days-Cu

(d) 28°C 50%RH MFG 6 Days-Ag

Figure 5-43 Effects of Temperature – Surface Geometry for Copper and Silver Coupons after Exposure 6 Days (AFM)



Figure 5-44 Effects of Temperature – Surface Roughness for Copper and Silver Coupons after Exposure 6 Days under NO₂+SO₂+O₃ (AFM)

5.4.3. Effects of Relative Humidity

For copper under $O_3+SO_2+NO_2$ exposure, increasing the relative humidity decreased the surface roughness and generated a smooth layer above the pure copper base uniformly [comparing (a) and (c) in Figure 5-26], which indicates a thicker average corrosion layer. For silver exposed to $O_3+SO_2+NO_2$, increasing the relative humidity from 50% RH to 80% RH with a temperature of 21°C resulted in larger convex dots, and increased the roughness of the silver surface [comparing (b) and (d) in Figure 5-45, Figure 5-46].



Figure 5-45 Effects of Relative Humidity – Surface Geometry for Copper Coupons after Exposure 6 Days (AFM, MFG: NO₂+SO₂+O₃)



Figure 5-46 Effects of Relative Humidity – Surface Roughness for Copper and Silver Coupons after Exposure 6 Days under NO₂+SO₂+O₃ (AFM)

5.5. Elemental Composition of the Corrosion Layer (XPS)

XPS spectra were obtained on a Quantum 2000 Scanning ESCA (Electron Spectroscopy for Chemical Analysis) microscopy (Physical Electronics, US) System, using Al radiation Ka=1486.6 eV with passing energy of 117.40 eV. Results from spectral acquisition were used to analyze chemical states of different elements (Cu/Ag C S O Cl N). Depth profile results provide information about spectral/element distribution at different depths from the surface. The copper and silver coupons analyzed by XPS were those after exposure to a pollutant mixture of $NO_2+SO_2+O_3+H_2S+Cl_2$ at 21°C and 50% RH for 25 days. Analyses were performed for three spots

located at the bottom, middle, and top of coupons to examine the spatial variability of corrosion product composition along the flow direction of the mixed gas flow.

Figure 5-47 shows the distribution of Cu element along the depth. From the depth profile, it shows that the bottom location has less Cu than at the top of the coupon, indicating that more Cu was replaced by the corrosion products at the bottom of the coupon, which is likely due to the thinner boundary layer there (leading edge of boundary layer flow over a flat plate). But there is not much difference between the top and middle, where the boundary layer thickness differs very little after a more fully developed boundary layer. So, there exists the corrosion gradient along the coupon as was observed previously with the color index method.



Figure 5-47 Depth Profile for Cu Element (Copper)

The elements C (Figure 5-48) and O (Figure 5-49) decrease with the depth, obviously reflecting that impurity and oxidization mainly occur on the surface. At about 10 nm, the coupon bottom has a higher level of O than that at the middle and top of the coupon, which again indicates a higher level of oxidization at the leading edge of the boundary layer.



Figure 5-48 Depth Profile for C Element (Copper)



Figure 5-49 Depth Profile for O Element (Copper)

The element S is distributed (Figure 5-51) uniformly until 10nm and the element Cl (Figure 5-50) increases slightly with the depth. The signal level for Cl is an order of magnitude higher than that of S. These indicate that both Cl_2 and H_2S play a role in corrosion, while Cl_2 has a more dominant effect than H_2S for copper.



Figure 5-50 Depth Profile for S Element (Copper)



Figure 5-51 Depth Profile for Cl Element (Copper)

The results (Figure 5-52) also show that at the outer layer of the copper coupon, the copper oxides compounds, Cu₂O, and CuO are the main products.



Figure 5-52 Copper Cu Spectrum Fit

There is more sulfite than sulfate, possibly indicating that the oxidation ability is not strong enough to cause all the sulfite to convert to sulfate (Figure 5-53).



Copper S Spectrum Fit

Figure 5-53 Copper S Spectrum Fit 136

More carbide than C with O, S, Cl, and N in Figure 5-54 are also observed, which indicates that some contamination occurred in preparing/polishing the coupons, perhaps due to the tool used.



Copper C Spectrum Fit

Figure 5-54 Copper C Spectrum Fit

Figure 5-55 shows the distribution of elements and the percentage of corrosion compounds for silver. From the depth profile, there is not much change after 20 nm.



As shown in Figure 5-56 the element C is mainly distributed near the outer layer of the corrosion products.



Figure 5-56 Depth Profile for C Element (Silver)

At the bottom of the coupon ("Down"), the level of element O decreases to zero at the 20nm depth (Figure 5-57).



Figure 5-57 Depth Profile for O Element (Silver)

The level of S approaches zero at the 60nm depth (Figure 5-58), indicating the significant role H_2S played in the corrosion because the level of S is so deep to reach the pure silver surface.



139

The elements Cl (Figure 5-59) and N (Figure 5-60) can be detected at even deeper depths (100+nm), indicating the effects of Cl_2 and NO_2 in the pollutant mixture on the corrosion product formation are important as the corrosion continued into the inner layer of material.



Figure 5-59 Depth Profile for Cl Element (Silver)



Figure 5-60 Depth Profile for N Element (Silver)

According to the spectra acquisition, at the outer layer of silver surface, there is much more sulfide than sulfite or sulfate (Figure 5-61).



Figure 5-61 Silver S Spectrum Fit

It was detected that more carbide than C with O, S, Cl, and N (Figure 5-62), similar to the results for copper.



Figure 5-62 Depth Profile for C Element (Silver)

5.6. Effect of Humidity Fluctuation

According to the temperature fluctuation data from the industry (Figure 5-61), the temperature fluctuation cycle at the inlet of the rack is 24 cycle/day and the standard deviation is 0.3°C.



Figure 5-61 Temperature Fluctuation

We used the temperature fluctuation cycle to predict the relative humidity fluctuation cycle. At 50%RH and 21°C, 0.3°C is converted to $\pm 5\%$ RH standard deviation and 24 cycle/day for relative humidity fluctuation. Two tests were performed with relative humidity fluctuations: 1) At 21°C and 50%RH, under NO₂+SO₂+O₃+H₂S+Cl₂, 5 exposure days (Figure 5-62); 2) At 21°C and 80%RH, under NO₂+SO₂+O₃, 6 exposure days (Figure 5-63). Information about monitoring data for exposure thermal condition is listed in Table 5-1.

No.	Temperature (°C)	Mean RH (%)	Standard Deviation of RH (%)	Pollutant Combination	Exposure Time (Day)
1	21	53	3.4	$NO_2+SO_2+O_3+H_2S+Cl_2$	5
2	21	83	3.27	NO ₂ +SO ₂ +O ₃	6

Table 5-1 Experiment Condition for Relative Humidity Fluctuation



Figure 5-62 Monitoring Data for 21° C and 80%RH Fluctuation



Figure 5-63 Monitoring Data for 21° C and 50%RH Fluctuation

Results from the coulometric reduction analysis are shown in Figures 5-64 and 5-65.



■21°C 50%RH ■21°C 70%RH ■21°C 80%RH ■28°C 50%RH

Figure 5-64 Effect of Relative Humidity Fluctuation – Copper Corrosion Results after Exposure 6 Days

For copper (Figure 5-64), corrosion thickness under the conditions with RH fluctuations were significantly larger than without relative humidity fluctuation. This could be due to both the fluctuation and a slight increase in the average relative humidity in both cases (about 83% and 53% RH, respectively).



Figure 5-65 Effect of Relative Humidity Fluctuation – Silver Corrosion Results after Exposure 6 Days

However, for silver Figure 5-65 shows that corrosion thicknesses under both relative humidity fluctuation conditions are lower than without relative humidity. This could be attributed to both the increase in the average relative humidity as well as the humidity fluctuation.

These results indicate that the RH fluctuation's effect on the corrosion has the same pattern as the effect of relative humidity. That is, either increasing relative humidity or having RH fluctuation would cause more copper corrosion for copper, but less corrosion for silver.

The observed color changes on the coupon surfaces (Figure 5-66) are also consistent with the above results from the coulometric reduction analyses. At 21°C and 80% RH fluctuation, the copper surface shows the corrosion dots, indicating a corrosion development process that is different from that at 21°C and 80% RH without fluctuation (in which a uniform layer of corrosion products was formed). For silver, at 21°C and 80% RH without fluctuation, it shows a darker color without RH fluctuation compared to the color of silver surface with fluctuation.

At 21°C and 50% RH without fluctuation, the surface of copper is more shining than it at 21°C and 50% RH with fluctuation, but this is not obvious for silver from the picture.



(a) 21°C and 80% RH Fluctuation

 $NO_2 + SO_2 + O_3$



- (a) 21°C and 50% RH Fluctuation
- (b) 21°C and 50% RH, no Fluctuation

 $NO_2+SO_2+O_3+H_2S+Cl_2$

 $NO_2 + SO_2 + O_3 + H_2S + Cl_2$





(b) 21°C and 80% RH, no Fluctuation

NO₂+SO₂+O₃



5.7. Effect of Voltage Bias (Electrical Current)

Figure 5-67 shows the color comparison for the effect of voltage bias. There were four exposure conditions:

- 1) 21°C 50% RH NO₂+SO₂+O₃
- 2) 21°C 50% RH NO₂+SO₂+O₃+Cl₂+H₂S
- 3) 21°C 80% RH NO₂+SO₂+O₃
- 4) 21°C 80% RH NO₂+SO₂+O₃+Cl₂+H₂S

For each exposure condition, two kinds of PCBs, one with bias and another without bias, were tested. In Figure 5-52, under the test conditions 2) and 3) above, the no bias PCB had a darker color than the PCB with bias. It shows that bias decreased the corrosion level, which might have resulted from the increase of temperature due to the current through the PCBs with the voltage bias.



Figure 5-52 Effect of Voltage Bias – Picture

That is consistent with the previous trend about temperature effect. Under conditions 1) and 4) above, the change in coupon color was not obvious.

SEM/EDS analysis was performed for the coupons, and results are shown in Figure 5-68.



3) 21°C 80% RH NO₂+SO₂+O₃+Cl₂+H₂S, Bias

4) 21°C 80% RH NO₂+SO₂+O₃+Cl₂+H₂S, no Bias



Figure 5-68 Effect of Voltage Bias – Backscattered Electron Micrographs for PCB after Exposure 6

Days (SEM)

- 1) 21°C 50% RH NO₂+SO₂+O₃+Cl₂+H₂S, Bias
- 2) 21°C 50% RH NO₂+SO₂+O₃+Cl₂+H₂S, no Bias

They represent the backscattered electron micrographs of PCB samples at different conditions. Overall, the 50% RH group (sample 1& sample 2) is less corroded than the 80% RH group (sample 3 & sample 4). This proves that the higher relative humidity caused more corrosion. Sample 1& Sample 2 may show some level of corrosion, however, it would be best to identify its existence with a control sample where there is no corrosion. The surface is predominately covered with Cu with some level of C and O. Sample 3 & 4 exhibit more corroded features. Brighter patches (less oxidized) and darker plate-like regions (more oxidized) show different levels of corrosion in sample 3. Corrosion in sample 4 shows more plate-lite oxidized features and fewer and smaller brighter patches compared to sample 3, indicating sample 4 was more corroded and the corrosion was more evenly distributed. This is consistent with the photo picture, which shows the voltage bias caused less corrosion on the coupon surface. Figure 5-69 also shows the element distribution on the PCBs. At 21°C and 50% RH under NO₂+SO₂+O₃+Cl₂+H₂S, the voltage-biased PCB has multiple elements (S, Al, Cu, Si, Cl, O, and C) detected. The presence of Al, Si, and C are likely deposits from the gas exposure. Elements are evenly distributed. But for the unbiased PCS under the same exposure condition, it only had chemical elements Si, O, Cu, and C, in which Si is likely from contamination.

1) 21°C 50% RH NO₂+SO₂+O₃+Cl₂+H₂S, Bias



2) 21°C 50% RH NO₂+SO₂+O₃+Cl₂+H₂S, no Bias



Figure 5-69 Effect of Voltage Bias – Chemical Elements Detection for PCB after Exposure 6 Days (EDS Mapping)

Representative EDS results of the biased PCB under 21° C, 50% RH and NO₂+SO₂+O₃+Cl₂+H₂S is shown in Figure 5-70. Spectrum 14's dark spots had Cu, C, O, Si identified, while spectrum 15's brighter spots have more Cu and less C, O. The dark region might have some corrosion.



Figure 5-70 EDS Spot Detection - 21°C 50% RH NO₂+SO₂+O₃+Cl₂+H₂S, bias

According to the picture and SEM/EDS analysis, PCBs with bias has lower corrosion than PCBs without bias. It may be caused by the increase of temperature due to the voltage bias. Increasing relative humidity caused more corrosion, which is consistent with the findings from the standard coupon test results discussed earlier.

5.8. Discussion

5.8.1. Corrosion Development over Time

According to the experimental results from the 30-day test at the reference condition (21°C and 50% RH for the five-compound gas mixture, $O_3+NO_2+SO_2+H_2S+Cl_2$), there exists a logarithmic relationship between the corrosion thickness and exposure time for copper. However, for silver, a linear relationship appears to be a better description of the corrosion development over the exposure time (Figure 5-1). For copper, after being exposed for a while, there may be a protection layer generated to inhibit further corrosion. This is not the case for silver; the corrosion thickness continues to build on the surface at the same rate.

5.8.2. Temperature Effect

Based on the results of the experiments, increasing the temperature from 21°C to 28°C at 50% RH leads to a significant reduction in the corrosion of copper, and some reduction in the corrosion of silver. When temperature increases, the chemical reaction rate constant is expected to increase because of increasing the reactivity of the ionization processes. But the corrosion rate also depends on the quantity of water and pollutant molecules being adsorbed on the material surface. For a

given relative humidity, an increase in temperature reduces the water molecules being adsorbed on the surface and may lead to a lower amount of pollutant deposition into the water adlayer, which would limit the corrosion rate. Franey et al. (1985) found that with increasing temperature, the water adlayer became thinner on the silver surface so that the dry sulfidation reaction became the main mechanism for corrosion. P. S. Mohan et al. (1991) also showed that temperature had different effects on steel, zinc, and copper corrosion. They pointed out that increasing temperature caused less corrosion at 80% RH and 100% RH for zinc which was in 0.1 liters SO₂ in the gas phase. But at 60% RH, it did not cause less corrosion at a higher temperature. So, the effect of the temperature on corrosion is complicated. Many confounding factors need to be considered, including temperature, relative humidity, quantity of water adlayer, pollutant levels, and their combinations. For our case, at 50% RH, the quantity of water adlayer may have been the more dominant factor.

5.8.3. Relative Humidity Effect

Relative humidity plays a key role in the corrosion process. When relative humidity was increased from 50% RH to 80% RH at 21°C, the corrosion thickness for copper increased dramatically for all the combinations of pollutants tested, but for silver the corrosion thickness decreased after increasing the relative humidity. There are many literature articles on the water vapor pressure effect on the corrosion rate (Vernon, 1931; T. Aastrup et al., 2000; Peter Eriksson et al., 1993; Per Backlund et al., 1996; P. S. Mohan et al., 1991). Vernon (1931) showed that when the relative humidity arrived at the critical relative humidity, the corrosion rate increased sharply for copper. In our experiments, when the relative humidity increased, the color of the copper coupon surfaces

was obviously much darker. Results from the AFM analysis revealed more densely packed corrosion spots (appeared to be a smoother surface) on the copper coupon than them on the silver coupon which had larger dots of corrosion products at 80% RH. This evidence supports the significant increase in corrosion thickness on the copper surfaces due to the increase of relative humidity from 50% to 80% RH at 21°C. Table 6-1 shows that for 21°C 80% RH with NO₂+SO₂+O₃, the copper EDS measurement showed more S on the surface than for 21°C 50%RH with NO₂+SO₂+O₃, but there was not much change for silver, which is consistent with the results from the coulometric tests.

When no Cl_2 or H_2S is present (i.e., only O_3 , NO_2 , and SO_2 were present), increasing the relative humidity from 50% RH to 70% RH did not cause any significant increase of corrosion thickness for copper but at 80% RH there was a significant increase in corrosion thickness. This suggests that a critical relative humidity condition exists between 70% and 80% RH above which corrosion would become much worse than the reference case regardless of the pollutant mixture. Hence data center environments should not operate at a relative humidity that is higher than 70% RH at 21°C. Table 6-1 Mass Fractions of Chemical Elements on the Coupon Surfaces under NO₂+SO₂+O₃

	A (concentra	Ag ation wt%)		Cu (concentration wt%)	
Element	Exposure Condition		Element	Exposure Condition	
	21°C 50% RH	21°C 80% RH		21°C 50% RH	21°C 80% RH
Ag	100	99.115	Cu	99.914	96.846
S	0	0.885	Ν	0.069	0
0	0	0	S	0.017	3.154

(Detected by EDS)

5.8.4. Individual and Synergistic Effect

Ozone is a chemical catalyst for the corrosion. Data on the ozone corrosion of copper and silver under more realistic concentration indoors (< 50 ppb) was lacking in the literature. Our experiments exposed the coupons to 60 ppb ozone. The results show that ozone alone did not cause any significant corrosion. All of the corrosion thicknesses measured at elevated temperature or RH conditions were essentially at the same level as that at the reference condition of 21°C and 50% RH.

For the two or three compound mixtures, SO_2+O_3 , NO_2+O_3 , $SO_2+NO_2+O_3$, the corrosion thicknesses did not differ significantly from one mixture to another and did not change with temperature for either copper or silver. The increase of relative humidity also did not affect the corrosion thickness for silver under these mixture conditions but did increase the corrosion thickness for copper. For copper exposed to 21°C and 50% RH, NO_2+O_3 had the highest corrosion thickness. When exposed to 21°C and 80% RH, SO_2+O_3 had the highest corrosion thickness. For

silver, these mixed gas combinations had similar corrosion thicknesses and did not vary significantly among the different combinations of compounds as was copper. Under a higher relative humidity (80% RH), sulfur dioxide resulted in the formation of copper sulfite. In theory, sulfur dioxide reacts with ozone in the liquid regime and ozone oxidizes the sulfur dioxide to H_2SO_4 then combines with copper to generate the CuSO₄. NO₂ dissolves in the liquid regime and results in HNO₂ being created. And it reacts with HNO₃ and Cu to produce the products of Cu₂O and HNO₂(gas). NO₂ also generates NO₂⁻ and NO₃⁻ after dissolving in liquid. These fundamental processes may explain the combined effects of SO₂, relative humidity, and temperature on the copper and silver corrosion under low SO₂ concentration in data center environment. Christofer Laygrad (2000) noted that NO₂ enhanced the formation of the sulfate ions through a catalytic mechanism, and O₃ enhanced the corrosion process through a stoichiometric reaction. The catalytic mechanism can increase the reaction rate but cannot produce additional products. And the stoichiometric reaction process resulted in additional reaction products as well as increased the reaction rate.

For the four compound combinations, $SO_2+NO_2+O_3+H_2S$, $SO_2+NO_2+O_3+Cl_2$, and SO_2+NO_2 + H_2S+Cl_2 , they show that hydrogen sulfide is the predominant corrosive gas for silver and chloride is the predominant corrosive gas for copper at the conditions of 21°C and 50% RH. But when the relative humidity was above 70% RH at 21°C, H_2S became very corrosive to copper. When silver is exposed to hydrogen sulfide, silver sulfide is formed. H_2S can also react directly with copper and O_2 to form copper sulfides. From Abbott's research (1988), under Class II environment: 10 ppb H_2S , 10 ppb Cl_2 , 200 ppb NO_2 , 70% RH, 20°C, chloride was the most critical element for reproducing the corrosion mechanism. The role of Cl_2 was to remove Cu_2O which then allows other pollutants to attack the Cu directly. When chlorine dissolves in the aqueous adlayer, it reacts to produce the chloride ions. And these ions can react with the copper, which causes the copper to dissolve into the liquid regime. When H₂S combines with Cl_2 , it causes even higher corrosion.

The five-pollutant compound combination, $SO_2+NO_2+O_3+H_2S+Cl_2$, was the worst case compared to other combinations for silver under all the thermal conditions. However, this was not the case for copper. The worst case for the copper at 21°C and 50% RH was for the $SO_2+NO_2+H_2S+Cl_2$ combination. It is possible that the addition of O_3 to the mixture may have helped in forming a protective layer for silver that ultimately slowed the corrosion. The fundamental underlying processes are not clear and need further investigation.

5.8.5. Effects of Humidity Fluctuation

The effects of humidity fluctuation on corrosion were evaluated by adding 10% RH fluctuation to two test conditions: 21 ° C & 80% RH with $SO_2+NO_2+O_3$ and 21 ° C & 50%RH with $SO_2+NO_2+O_3+H_2S+Cl_2$. Results from the coulometric reduction analyses have shown a significant increase of corrosion in the copper coupons due to the added humidity fluctuation for both cases, but not for silver. This is consistent with the trend that an increase in RH beyond 70% RH would increase the corrosion of copper even when exposed to the three pervasive compounds $(SO_2+NO_2+O_3)$. In addition, when Cl_2 is present as in the five compound MFG test case, an increase in RH beyond 50% RH increased the corrosion of copper. For silver, the added 10% RH fluctuation also increased the average RH the coupons were exposed to, which might be partially responsible for the reduction in the corrosion observed.

5.8.6. Effects of Voltage Applied to the PCBs

Based on the color index approach, the voltage bias on the test specimen decreased the corrosion rate, likely due to the increase in the PCB temperature due to joule heating. Results from the XPS analysis also confirmed the reduction in corrosion due to the voltage bias on the PCBs. A coulometric analysis apparatus suitable for the PCB coupon analysis will be set up in the near future to provide a quantitative assessment.

5.9. Conclusions

The following findings can be summarized from the present study:

- O₃, NO₂, and SO₂ are pervasive pollutants in data center environment, while the presence of Cl₂ and H₂S are more of a local phenomenon depending on the activities inside and surrounding specific data centers. Hence separate thermal design guidance should be established for Cl₂ and H₂S.
- 2) Corrosion development over time: According to the experimental results from the 30-day tests (21°C 50% RH for the five-compound gas mixture, O₃+NO₂+SO₂+H₂S+Cl₂), there exists a logarithmic relationship between the corrosion thickness and the exposure time for copper. However, for silver, a linear relationship appears to be a better description of the development

of the thickness over the exposure time and increasing the relative humidity leads to a reduction in the corrosion rate.

- 3) Effects of pollutant mixture: For the reference temperature and RH condition (21°C and 50% RH), a significant copper corrosion occurred only for the Cl₂-containing MFGs (mixtures of NO₂+SO₂+O₃+Cl₂ and NO₂+SO₂+Cl₂+H₂S, and NO₂+SO₂+O₃+Cl₂+H₂S). These results suggest that Cl₂ had the most corrosive effect for copper. Without Cl₂ the corrosion thicknesses were significantly lower. However, for silver, significant corrosion occurred only when H₂S was in the pollutant mixture. The dominating effect of Cl₂ on copper corrosion and that of H₂S on silver corrosion were also evidenced from the corrosion products or elements identified from the results of coulometric reduction, SEM/EDS, AFM, and XPS analyses. As a result, separate design guidelines could be established for data center environment depending on whether there is Cl₂ and/or H₂S in the environment one for the environment where only the pervasive compounds (O₃, NO₂, and SO₂) in atmospheric pollution are present, and the other where Cl₂ and/or H₂S are also present due to local surrounding and indoor activities.
- 4) Effects of relative humidity:
- a) For copper, increasing the relative humidity from 50% RH to 70% RH while keeping the temperature at the reference condition (21°C) enhanced the corrosion when Cl₂ was present, but did not have a significant impact on corrosion when Cl₂ was not present. A further increase of the relative humidity to 80% RH resulted in significant corrosion for all gas conditions tested including O₃, SO₂+O₃, NO₂+O₃, NO₂+SO₂+O₃, NO₂+SO₂+O₃, NO₂+SO₂+O₃+Cl₂,

 $NO_2+SO_2+O_3+H_2S$, and $NO_2+SO_2+O_3+Cl_2+H_2S$. This suggests that a critical relative humidity exists for copper between 70% RH and 80% RH, above which the corrosion thickness would increase dramatically.

- b) For silver, however, increasing the relative humidity did not cause a significant increase in the corrosion thickness for all gas conditions tested, especially for the five-compound mixture in which increasing the relative humidity from 50% RH to 70% RH and then to 80% RH even resulted in a reduction in the corrosion thickness.
- c) As a result, for data center environments where only the pervasive three compounds are present, relative humidity as high as 70% RH at 21°C is acceptable for copper and silver corrosion control.
- 5) Effects of temperature:
- a) For copper, increasing the temperature from 21°C to 28°C while keeping the relative humidity at the reference condition (50% RH) dramatically reduced corrosion thickness for all mixture conditions tested. This was unexpected, but a repeat test confirmed the observation. It was likely that at a higher temperature, a much lower amount of pollutants (especially Cl₂) could be adsorbed or absorbed on the test coupon's surface to cause corrosion.
- b) For silver, significant corrosion thickness was still detected at 28°C and 50% RH for the H₂S containing mixture conditions. The elevated temperature had no significant impact on silver corrosion when H₂S was not present.
- c) As a result, for data center environments where Cl₂ and H₂S are not present, temperature as high as 28°C is acceptable for corrosion control if the relative humidity is at or below 50% RH.

- 6) Effects of humidity fluctuation:
- a) Adding 10% RH fluctuations to the test case of 80% RH at 21°C with the three pervasive compounds (NO₂, SO₂, and O₃) and the test case of 50% RH at 21°C with the five compounds (NO₂, SO₂, O₃, Cl₂, and H₂S) significantly increased the corrosion of copper and reduced the corrosion of silver.
- b) This is similar and consistent with the effects of the average relative humidity on the corrosion of copper and silver. Both the fluctuation and the 3% RH increase in the average relative humidity may be responsible for the changes in the corrosion thickness.
- 7) Effects of voltage bias (electrical current):
- a) Results from both the color index screening method and SEM/EDS analysis show that the voltage bias on the PCBs reduced the corrosion.
- b) The current carrying copper traces raised the temperature slightly thereby probably affected the level of corrosion, similar to what was seen in higher temperatures for testing of the copper coupons, which is consistent with the temperature effect measured by the standard copper coupon tests. PCBs with bias have less corrosion than PCBs without bias.
- 8) Results from the SEM/EDS, AFM, and XPS analyses gave supportive information about the corrosion products and geometry of corrosion surface regarding the effects of different factors such as temperature, relative humidity, pollutant combinations, and electrical current on the corrosion level. They also suggested that different corrosion development processes and mechanisms may exist depending on the compound mixture, temperature, and humidity

conditions. A further and more in-depth investigation is needed to develop a better understanding and prediction models.

9) The color index method developed can distinguish between severe (> 1000 Angstroms) and low (< 500 Angstroms) corrosion conditions, and hence can be used as a screening tool, though no definitive correlations can be established between the corrosion thickness and the relative RGB values of the coupon surfaces.

6. Corrosion Model Development

6.1. Introduction

Numerous laboratory studies have focused on the temperature, relative humidity, and gas contaminations effects on corrosion. However, most of them have been conducted for extremely high concentrations of gas pollutants, much higher than even concentrations expected outdoors. Recent results from ASHRAE 1755-RP (Zhang, Zhang, Schmidt, Gilbert, & Guo, 2019) show that even at relatively low concentrations (e.g., 10 ppb H₂S, 80 ppb NO₂, 40 ppb SO₂, 2 ppb Cl₂, and 60 ppb O₃), the synergistic effects of O₃, NO₂, SO₂, and/or H₂S/Cl₂ can cause high corrosion levels that are much higher than the limits set for data center operation: 300 Angstroms/month for copper and 200 Angstroms/month for silver. However, currently there is no simulation model that is capable of predicting the synergistic effects of the different contaminants, relative humidity, and temperature. In this chapter, a mechanistic corrosion model is developed for data center environment.

6.1.1. Key Influencing Factors

Atmospheric corrosion of metals is a complex process. The components of corrosion system being investigated include corroded metal, deposition, adsorbed water in/on the deposition as the electrolyte for the electro-chemical process, and gas containing pollutants and moisture. Corrosion is an electro-chemical process consisting of two half-cell reactions, an oxidation of metal, and a reduction reaction of water, hydrogen, or oxygen gas. In our model, the backward half-cell reaction is ignored. Key influencing factors include:

- Thermal environmental conditions (humidity and temperature). Humidity has an influence on the thickness of adsorbed water layer which affects the properties of solid phase (deposition), diffusion of species in the electrolyte, and concentration of each reactant. Temperature affects the chemical reaction rate and the adsorption of chemical species and water vapor on the metal surfaces, as well as the diffusion of chemical species through the corrosion product layer.
- Pollutants in the air (species and their concentration levels). The mechanism of chemical reaction depends on the category and concentration level of pollutants in the air.
- Deposition of corrosion (density, conductivity, porosity, and adsorption of moisture). The bare metal which is exposed to the pollutant is with the initial protection oxide layer as an initial corrosion barrier. If there exist pollutants later, other deposition will be generated. So, the characteristics of this protection oxide layer and further deposition generated will have a major impact on the corrosion rate.
Corrosion in data center equipment is a slow process due to relatively low pollutant concentrations and controlled temperature and humidity environment. A relatively long exposure time is needed to observe apparent corrosions. Field coupon-based corrosion tests typically require 30 days of exposure of the test specimens. During the long exposure period, fluctuations in the temperature, humidity, and pollutant concentrations will affect the cumulative exposure of the materials and the corrosion development over time.

6.1.2. Empirical Models

Before discussing the details of each kind of empirical models, corrosion mechanism on which the empirical model relies is to be the first question needed to be understood. For the electro-chemical process, the energy change of the half-cell reaction is the driving force for the chemical reaction. The electric field generated by these half-cell reactions also affects the ion migration through the region of oxide formation. As shown in Figure 6-1, each half cell chemical reaction occurred at a different interface. One oxidation reaction is at the oxide-oxygen interface, and a reduction reaction is at the metal-oxide interface. There are three factors which limit the corrosion process: chemical reaction at the oxide-oxygen interface.



Figure 6-1 Schematic Diagram of Oxidation (Shackelford, 1992)

The categorization of empirical models is based on the dominant limiting process in the corrosion. Three common kinetic laws have been established for predicting the oxidation rate: parabolic equation, linear equation, and logarithmic equation.

1) For parabolic equation, it is given by:

$$y^2 = kt + C, \tag{1}$$

where y is the corrosion thickness, t is the exposure time, k is the rate constant (related to the partial pressure of oxygen, not to chemical properties of oxygen and metals), and C is the constant. This model is applicable under the following conditions:

- Metal is exposed to high temperature.
- Corrosion thickness is higher than 10⁴ Angstroms.

• Limiting process for the corrosion: Diffusion of ions and migration of electrons in the oxide regime.

In this parabolic model, the positive metal ions migrate to the oxide-oxygen interface. Their migration velocity is proportional to the strength of the electric field formed near the oxide-oxygen interface because of the reduction of oxygen.

2) For linear equation, it is shown by:

$$y = kt + C, \tag{2}$$

This model is used for the condition under which the chemical reaction at the metal-oxide interface is the dominant factor of the corrosion process.

3) For logarithmic equation, it is represented by:

$$y = k_0 \ln\left(\frac{t}{\tau'} + 1\right),\tag{3}$$

where k_0 and τ' are coefficients. The derivation of the logarithmic equation is from Poisson's relation and kinetics of chemical reaction.

This model works for the conditions as below:

- Metal is exposed to low temperature.
- Corrosion thickness is lower than 10⁴ Angstroms.
- Limitation of corrosion: chemical reaction at the metal-oxide interface.

When the oxide regime is the thin film (limiting film thickness) and the temperature is lower than the critical temperature which affects the characteristic of crystal metal oxide and oxidation rate, the migration velocity of metal ions is proportional to the exponent of electric field strength and chemical reaction rate at the metal and oxide interface.

6.1.3. Mechanistic Models

A more comprehensive and capable corrosion model is needed to predict the corrosion levels under different pollutants and thermal environmental conditions in support of the design and operation of data centers in an energy efficient manner while reducing the risk of pre-mature failure of datacom equipment due to corrosions. There are two main parts which are needed to be described for mechanistic models: the physical process (mass transfer of the species and migration of charged ions) and the chemical process (chemical reactions). Because of the complication of corrosion mechanism, it is necessary for mathematic models to be simplified.

1) The GILDES model

From the multi-regime perspective on corrosion chemistry, Graedel identified the six regimes (Figure 6-2) as the conceptual framework of corrosion: G (gas), I (interface), L (liquid), D (deposition layer), E (electrode regime) and S (solid) (Grardel, 1996). 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. The simplification adopted in this model is to mimic the adsorbed thin adsorbed/liquid film by using bulk aqueous chemistry.



Figure 6-2 A Schematic Representation for the Six Regimes and the Transitions and Transformation (Grardel, 1996)

<u>G (Gas) layer</u>: The rate of change of each species' concentration in the gas regime is governed by the continuity equations, which includes entrainment and detrainment of the species across the top and bottom boundaries of the regime, the loss of the reactants, and the increase of the product due to the chemical reaction and horizontal advection as the Figure 6-3.



Figure 6-3 A Schematic Diagram of the Basic Elements in the GILDES Model for the Gaseous Regime (Grardel, 1996)

For each chemical reaction, the rate constants are used for the reaction rate which is temperaturedependent in the Arrhenius form. Some corrosion reactions are affected by the solar radiation, which introduced the new terms for photolysis rate. Some simplifications are allowable in this regime and more focus is placed on the aqueous chemistry. Thus, certain simplified models ignored this effect. Another simplification approach is to consider the constant concentration of each species in this regime, which avoids calculating the transport and reaction effects.

<u>I (Interface) Layer</u>: The species in the gas regime are across the interface into the liquid phase. Then, the equilibrium distribution of the species between the liquid and gas phase is described by Henry's law. The concentration of a gas $[M_i]$ in a liquid can be transformed by using the Henry's law coefficient H_i and the partial pressure of the gas p_i :

$$[M_i] = H_i p_i.$$

The value of the Henry's law coefficient is dependent on the specific situations, which include the transformation of dissolved gases, adsorption and desorption, the volatility, temperature, pH, etc.

<u>L (Liquid) Layer</u> – The species in the gas phase are transferred into the liquid regime. The concentrations of species in this regime not only use the time-dependent mass transfer like in the gas regime, but also need the activities of the species a_i , which replaces the concentrations in the chemical reaction in the gas regime and are defined by multiplying the concentration $[M_i]$ by the activity coefficients γ_i using the Davies' expression:

$$log\gamma_{i} = -CZ_{i}^{2} \left(\frac{\mu^{\frac{1}{2}}}{1 + \mu^{\frac{1}{2}}} - 0.3\mu \right),$$

where C is a constant related to the dielectric properties of the solvent, μ is the ionic strength dependent on the molality, and Z is the ionic charge.

This regime is the soul of the GILDES model. There are three important transformations: protolytic reaction (diffusion-controlled, rate constants $10^{10} - 10^{11}M^{-1}s^{-1}$), oxidation-reduction reaction (drate constants $10^5 - 10^9M^{-1}s^{-1}$), and the dissolution and precipitation of solid phase.

<u>D (Deposition) Layer</u>: Formation of corrosion layers and natural minerals cover the metal surface. The chemical and physical steps are involved in these formation processes. The rate of growth of nucleation is considered, which controls the overall crystallization rate. When the surface control is the domain limitation, the rate of growth $R_G(mol \ cm^{-2} \ s^{-1})$ is given by:

$$R_G = k_G (\Delta c - 1)^{n'}, \qquad (\Delta c > 1)$$

where k_G is the empirically-defined effective rate constant for crystal growth, Δc is the degree of supersaturation of the product species dependent on the concentrations of ion activity product and solubility product, and n' is an order parameter dependent on crystal size and morphology. Besides, the ion transport in deposition layer is included, which has an influence on the permeation of reactive species through this layer into the metal surface and the transportation of dissolved compounds outward to the liquid phase.

<u>E (Electrodic) Layer</u>: The electrochemical reaction occurs in this regime. The corrosion rate is defined by the Butler-Volmer equation:

$$i = i_0 \left[\exp\left(\frac{\alpha nF}{RT}\eta\right) - \exp\left(\frac{-\beta nF}{RT}\eta\right) \right],$$

where *i* is the current density, η is the overpotential, i_0 is the exchange current density, α and β are the transfer coefficients of the forward and backward reactions, *n* is the electrons transferred, R, T, and F are the gas constant, temperature, and the Faraday constant.

Solid - The metal dissolves into the deposition regime after chemical reactions. The dissolution rate is given by:

$$R_{diss} = k_{diss} x_a P_i S_i$$

where R_{diss} is the proton- or ligand-promoted dissolution rate, k_{diss} is the rate constant, x_a is the mole fraction of dissolution active sites, P_j is the probability of finding a specific site in the coordinative arrangement of the precursor complex, and S is the surface concentration of sites.

<u>S (Solid) Layer:</u> At the beginning of corrosion, the liquid layer attaches to the surface of the solid layer. It causes the dissolution of solid by the oxidation reaction.

It is a very good conceptual framework for the corrosion process and also gives a guide to mimic the field corrosion. But the limitations of this GILDES model are no considerations of the passivity of corrosion product and the effects of relative humidity and electrified.

In order to simplify the model, some authors (Sun, et al., 2007; Clarelli, et al., 2014) chose to neglect the interface, liquid, and electrodic regimes. Payer added the porous layer between the liquid regime and deposition regime which was the initial protective oxide layer (Payer, Ball, Rickett, & Kim, 1995). Tidblad used this model to study the SO₂ effect on the aqueous copper corrosion (Tidblad & Graedel, GILDES Model Studies of Aqueous Chemistry. III. Initial SO2induced Atmospherc Corrosion of Copper, 1996). The copper was exposed at room temperature under 80% relative humidity and 210 ppb sulfur dioxide. This study assumed the interface regime was infinitely thin and the electrodic regime was neglected. For the chemical reaction, the dissolution rate of the copper depended on the hydrogen ion concentration. Besides, the protonpromoted and ligand-promoted dissolution were considered in this model. The results showed the corrosion products were Cu₂SO₃, CuSO₃, and Cu₂O. After a few years, Tidblad et. al (2005) studied the synergistic effects of 200 ppb SO₂ with either 200 ppb NO₂ or 0-250 ppb O₃ on copper at room temperature under 80% relative humidity by using the GILDES mode. The calculation showed the prediction of nitrate formation in SO_2+NO_2 mixture in this model was poor. Besides, the sulfate formation in $SO_2 + O_2$ mixture was affected by the pH value of the liquid phase.

In the GILDES model, there was a common assumption that the liquid layer was infinitely thin so that there was no concentration gradient of each species in it. However, the thickness of adsorbed liquid layer varies with the relative humidity for atmospheric corrosion. It has a huge impact on the concentration of reactants on which the corrosion rate depends. Venkatraman et. al. proposed a model which simulates the corrosion for iron covered by a thin layer of NaCl electrolyte (Venkatraman, Cole, & Emmanuel, 2011). They considered the concentration gradient of oxygen in the electrolyte and assumed the pseudo-steady state diffusion of oxygen. Their model only had three phases: gas, liquid, and solid. It considered the oxygen diffusion through the salt solution and combined the Butler-Volmer equation to calculate the corrosion products as a source/sink term for ionic species transport. Furthermore, they accounted for the effects of oxide products including the porosity and oxide conductivity.

2) The MITReM model

In 1996, Bortels et al. proposed multi-ion transport and reaction model (MITReM) which not only included the mass transfer of the species, but also accounted for the migration of the charged species (Bortels, Deconinck, & Bossche, 1996). There are two main conservations to describe this transport phenomenon of mass and charge in the liquid layer: mass conservation and charge conservation.

• Mass Conservation:

The dilute species i transfers in the liquid layer due to diffusion, convection, and migration. The flux N_i of any species i is given by:

$$\boldsymbol{N}_i = -\boldsymbol{D}_i \boldsymbol{\nabla} \boldsymbol{c}_i + \boldsymbol{c}_i \boldsymbol{\nu} - \boldsymbol{z}_i \boldsymbol{u}_i \boldsymbol{F} \boldsymbol{c}_i \boldsymbol{\nabla} \boldsymbol{\emptyset}, \tag{4}$$

where D_i is the diffusion coefficient, c_i is the concentration of species in the solution, \boldsymbol{v} is the velocity of the liquid solvent, z_i is the charge of species, u_i is the mobility, F is the Faraday constant, and $\boldsymbol{\emptyset}$ is the electronic potentials in the electrolyte. Some studies ignored the convection effect. The mobility u_i can be replaced by $\frac{D_i}{BT}$ in terms of the Nernst–Einstein equation.

The continuity equation for any species is expressed by:

$$\frac{\partial c_i}{\partial t} = -\nabla \cdot N_i + R_i, \tag{5}$$

where R_i is the production rate of species due to the chemical reaction. After substituting (4) into (5), we obtain:

$$\frac{\partial c_i}{\partial t} = -\nabla (-D_i \nabla c_i + c_i \nu - z_i u_i F c_i \nabla \phi) + R_i.$$
(6)

• Charge Conservation:

In the liquid layer, the total electrical charge never changes, which means the amount of positive charge is always equal to the amount of negative charge in this isolated field. The charge conservation is given by:

$$\frac{\partial \rho}{\partial t} + \sum_{i} \nabla \cdot \mathbf{N}_{i} = 0, \qquad (7)$$

$$\rho = F \sum_{i} z_i c_i = 0, \text{ (electroneutrality)}$$
(8)

where ρ is the density of freely moving charge (the amount of electric charge per unit length, surface area, or volume). The first term represents the rate of change of the charge density at a point. The second term denotes the charge flux moving in and out of the field.

So, combine (4), (7) and (8), we can get:

$$0 + \sum_{i} \nabla \cdot (-D_i \nabla c_i + c_i \nu - z_i u_i F c_i \nabla \emptyset) = 0.$$
(9)

If ignore the convection effect, equation (9) can be simplified as:

$$\sum_{i} \nabla \cdot (-D_i \nabla c_i) = \sum_{i} \nabla \cdot (z_i u_i F c_i \nabla \phi) = 0.$$
(10)

Wen Sun et.al. used MITReM to simulate the formation of calcareous deposits on steel in seawater (Sun, Liu, & Li, 2012). This model included three regimes: liquid layer, deposition layer, and solid parts as shown in Figure 6-4.



Figure 6-4 Schematic of the Formation of Calcareous Deposits in the Diffusion Layer and 1D Geometry (Sun, et al., 2012)

In this model, they assumed the reaction occurred only on the uncovered steel surface, and tortuosity and relative permittivity of the deposits were constant. In Figure 6-5, the corrosion thickness increased with time as a logarithmic relationship. The growth rate was very large at the beginning stage, but then jumped to lower values.



Figure 6-5 Changes of the Thickness and Growth Rate of Calcareous Deposits with Time (Sun, et al., 2012)

Besides, the coverage rate and electric resistance increased, and the porosity of the products decreased. Deconinck et al. (2012) also studied the electrochemical machining process by using MITReM and obtained the temperature distribution and shape evolution (Deconinck, Damme, & Deconick, 2012).

MITReM considered the molecular transfer and electric field effect but did not include the characteristics of corrosion products (porosity, conductivity of this semi-conductor, and density). In 2011, Venkatraman et.al. not only considered the mass and charge conservations but also studied the porous corrosion product effect. Their model simulated the corrosion of iron under a thin porous oxide film filled with NaCl moisture in Figure 6-6. It used the Butler-Volmer equation to model the chemical reactions.



Figure 6-6 Corrosion of a Metal Surface under a Thin Oxide Film Filled with Moisture and of Thickness (L) (Venkatraman et.al., 2011)

The dissolution of metal only occurred on the metal surface but the reduction of oxygen on the uncovered metal surface and the oxide surface. The electrons lost from the metal surface. Some

parts of them transferred through the metal into the oxide film and got captured by the oxygen. The rest existed on the metal surface to support the reduction of oxygen (Figure 6-7).



Figure 6-7 Corrosion Mechanism (Venkatraman et.al., 2011)

The results showed the corrosion rate (current density) decreased with the increasing thickness of oxide products (Figure 6-8).



Figure 6-8 Corrosion Rate Varied with the Thickness of Oxide Product (Venkatraman et.al., 2011)

It also showed not only the porosity effect (Figure 6-9) but also the oxide conductivity effect (Figure 6-10). The higher porosity enhanced the corrosion process, which gave more space to transfer the species and chemical reactions. Even though the higher oxide conductivity made the corrosion worse, it still did not show much difference under the different conductivity.



Figure 6-9 Effect of Porosity of Oxide (Venkatraman et.al., 2011)



Figure 6-10 Effect of Oxide Conductivity (Venkatraman et.al., 2011)

These authors used the MITReM model as the base and included more corrosion factors into the model, such as the tortuosity, relative permittivity, porosity, and conductivity of oxide products. It suggested that the characteristics of corrosion products were very important factors during the corrosion process. But there have been very few studies on the features of oxide products. There is no evidence on how the characteristics of oxide products vary with time.

Besides, these studies assumed the oxide layer was constant without the change in thickness, which is contrary to the actual development of the corrosion layer. Clarelli et al. created a model to predict the corrosion development (Clarelli, Filippo, & Natalini, 2014). In their model, they provided the prediction of the evolution of copper corrosion products (brochantite and cuprite) under sulfur dioxide pollutant in Figure 6-11. The molar ration in reaction between reactant and product described the chemical reaction rate.



Figure 6-11 Cuprite and Brochantite Deposition on Copper (Clarelli, Filippo, & Natalini, 2014)

This model focused on two regimes: solid layer and deposition layer. It described the concentrations of SO_2 , water, and oxygen throughout the brochantite and cuprite by using the Fick's law and mass balance. It assumed the copper was exposed under 100% relative humidity and the chemical reactions were instantaneous. The feature of this model not only included the development of corrosion products but also considered the consumption of metal itself in Figure 6-12.



Figure 6-12 Cuprite and Brochantite Theoretical Growth (in Time) on Copper (Clarelli, Filippo, & Natalini, 2014)

3) Deposition layer-centric model

Instead of predicting the chemical species transfer, there is another kind of model to simulate the transport of the charged lattice defects (electron holes and metal vacancies) throughout the oxide products. It made use of the characteristic of corrosion products and focused on the deposition layer. For example, Cu₂S and Cu₂O are p-type semiconductors which are deficient. In this model, it still used the continuity equation to describe the electron holes and metal vacancies in the deposition layer and combined it with Poisson's equation to simulate the electric field. Larson developed a new model to predict the copper corrosion by SO₂ pollution, which analyzed the Cu₂S development in time by simulating the copper vacancies and electron holes transport in Figure

6-13 (Larson, 2002). His model focused on three main regimes: gas layer, deposition layer, and solid layer. It assumed the chemical reaction occurred at the two top (y = L) and bottom (y = 0) boundaries of Cu₂S and ignored the adsorbed liquid layer. It made use of chemical reaction coefficient to represent the reaction rate.



Figure 6-13 Schematic of Copper Sulfidation Model (Larson, 2002)

After solving the asymptotic solution by using a nonlinear equation solver (the standard SLATEC routine DNSQE), he got the growing of sulfide layer which is shown in Figure 6-14.



Figure 6-14 Fit to Copper Sulfidation Rate Data. Points were experimental measurements and curves were from the model. (a) 400, (b) 200, and (c) 40 ppb (Larson, 2002)

The results showed that increasing the concentration of H_2S to which copper was exposed made the corrosion worse. When the concentration of pollutant was low, the relationship between the sulfide layer thickness and exposure time was closed to linear. Moreover, Sun et. al. applied a similar method to model the pore corrosion model for gold-plated copper contacts (Sun, Moffat, Enos, & George, 2007).

Most of the corrosion models did not consider the relative humidity effect and assumed the liquid layer fully covering the metal surface. However, relative humidity is a very important factor in atmospheric corrosion. It not only affects the mass transfer of species through the adsorbed water layer, but also affects the chemical reaction rate. There is a knowledge gap for the relative humidity effect.

- For existing corrosion mathematical models, they started by only considering the mass transfer of species and chemical reactions, and then included the electric field effect. After having more knowledge of the p-type characteristics of oxide products, the study of corrosion came to the new stage to account for the transport of charged lattice defects in the deposition layer-centric mechanistic model. There are some challenges for developing the mechanistic corrosion models;
- 2) It takes huge effort to get a numerical solution of the coupled partial differential equations;
- 3) There is a lack of knowledge of more complicated chemical reaction processes over time;
- 4) The characteristics of depositions need to be further studied;
- 5) The parameter data for diffusion and chemical kinetic are lacking.

In the present study, we further develop and apply the MITReM model to simulate the corrosion development and analyze the effects of humidity and temperature on the corrosion due to exposure to mixture pollutants containing Cl_2 .

6.2. Model Development

In this section, we present the details of model development including the corrosion system representation, assumptions, governing equations, boundary conditions, initial conditions, methods for the determination of the model parameters, model implementation, and verification.

6.2.1. System and Assumptions

This section covers the description of our mathematical model from two aspects: corrosion system representation and modeling assumptions.



Figure 6-15 Schematic of the Corrosion System Modeled: (a) Chemical Species Transfer; (b) Current Density and Electron Migration

As shown in Figure 6-15, there are three main layers in the corrosion system modeled: gas layer, initial deposition layer filled with the adsorbed water, and copper solid layer. The initial thickness of porous copper oxide is L above the copper top surface (y = 0). The chloride gas adsorbed by the water layer at y = L fully reacts with water and generates Cl⁻ ions which transfer throughout the electrolyte (copper oxide layer) to the top surface of the copper. After that, the copper is oxidized by these Cl⁻ ions: Cu + 2Cl⁻ \rightarrow CuCl⁻₂ + e⁻. The oxygen from the gas layer diffuses through the adsorbed water layer to the metal surface. Then oxygen is reduced into OH⁻ ions which diffuse into the electrolyte: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$. Then, two chemical products pass into the electrolyte and react to generate the copper oxide as the deposition on the top of metal surface: $2CuCl^-_2 + 2OH^- \rightarrow Cu_2O + H_2O + 4Cl^-$.

Further, we assume that:

- The adsorbed chloride gas fully reacts with water at y = L;
- The thickness of porous copper oxide varies with time but is assumed to be constant within a sufficiently small time step.
- The two half-cell reactions occur at the metal surface (y = 0) under the neutral electrical charge condition.
- The effect of electric field and convection effect are ignored in the very thin electrolyte.
- In each half-cell reaction, the backward reaction is ignored, and the dominant reaction direction is forward.

- In every time step, the oxygen and chloride ions are considered to arrive at the pseudosteady state of diffusion in the adsorbed water layer.
- The corrosion product is only generated at the metal surface (y = 0).
- The hydrolysis of copper ions and self-hydrolysis of H₂O are not included in this model.

6.2.2. Governing Equations

6.2.2.1. Kinetics of chemical reaction

The copper dissolution rate expression – current density $i_{Cu|CuCl_2^-}$ (Bacarella, Griess, & Jr., 1973) is:

$$i_{Cu|CuCl_{2}^{-}} = \frac{zFD_{CuCl_{2}^{-}}}{L} c_{Cl}^{2} |_{y=0} e^{\frac{F(E_{corr} - E_{Cu|CuCl_{2}^{-}})}{RT}},$$
(11)

where z is the charge transferred in the metal reduction (z = 1), F is the Faraday's constant, $D_{CuCl_2^-}$ is the diffusion coefficient for $CuCl_2^-$ (cm²/s), L is the thickness of copper oxide (cm), $c_{Cl^-}|_{y=0}$ is the concentration of Cl^- at the copper surface (mol/cm³), E_{corr} is the corroding system potential (V), $E_{Cu|CuCl_2^-}^0$ is the standard reduction potential for metal dissolution reaction (V), R is the gas constant, and T is the absolute temperature (K).

The current density $i_{O_2|OH^-}$ for oxygen reduction is presented by the Butler-Volmer expression (Venkatraman, Cole, & Emmanuel, 2011):

$$i_{O_2|OH^-} = -i_{O_2|OH^-}^0 \exp\left[\frac{-n\alpha_{O_2|OH^-F}}{RT} \left(E_{corr} - E_{O_2|OH^-}^0\right)\right] \frac{c_{O_2}|_{y=0}}{c_{O_2}^{sat}},$$
(12)

where $i_{O_2|OH^-}^0$ is the corresponding exchange current density (A/m²), *n* is the obtained electrons from the copper oxidization (*n* =1), $\alpha_{O_2|OH^-}$ is the transfer coefficient, $E_{O_2|OH^-}^0$ is the standard reduction potential for oxygen reduction, $c|_{y=0}$ is the concentration of oxygen at the metal surface (mol/m³), $C_{O_2}^{sat}$ is the saturation concentration of oxygen at y = 0 (mol/m³).

According to the neutrality of the whole electrolyte, it is shown by:

$$-i_{O_2|OH^-} = i_{Cu|CuCl_2^-} = i_{corr}.$$
 (13)

6.2.2.2. Diffusion of oxygen and chlorine ion

In the electrolyte, the transfers of oxygen and chlorine ion follow the Fick's Law:

$$\frac{\partial^2 c_i}{\partial y^2} = 0, \qquad (i = 1, 2) \tag{14}$$

where $1 = O_2, 2 = Cl^-$.

Boundary conditions:

At y = 0,

$$-D_{O_2}\frac{\partial c_{O_2}}{\partial y}|_{y=0} = \frac{i_{O_2|OH^-}}{F} = \frac{i_{corr}}{F},$$
(15)

$$-D_{Cl} - \frac{\partial c_{cl}}{\partial y}|_{y=0} = \frac{i_{Cu|CuCl_2}}{F} = \frac{i_{corr}}{F}.$$
(16)

At y = L,

$$c_i|_{x=L} = c_i^{sat}. (17)$$

6.2.2.3. Transport of chemical species

After each half-cell reaction, the transfers of OH^- and $CuCl_2^-$ are described by:

$$\frac{\partial c_i}{\partial t} = D_i \frac{\partial^2 c_i}{\partial y^2}, \qquad (i = 3, 4)$$
(18)

where $3 = CuCl_2^-$, $4 = OH^-$.

At y = 0,

$$-D_i \frac{\partial c_i}{\partial y}|_{y=0} = \frac{i_{corr}}{F}.$$
(19)

At y = L,

$$-D_i \frac{\partial c_i}{\partial y}|_{y=L} = 0.$$
 (20)

The initial condition which is gained from the calculation of equations system (11) - (16):

$$c_i(y,0) = c_i^{init} = c_i^{sat}$$
. (21)

6.2.2.4. Non-dimensionalization

Table 6-1 lists the non-dimensional parameters:

Table 6-1 Non-dimensional Parameters

$\xi = \frac{y}{L_0},$ L_0 – initial thickness of Cu_2O	Non-dimensional vertical coordinate
$\tau = \frac{tD_{O_2}}{{L_0}^2}$	Non-dimensional time
$\theta_i = \frac{c_i}{c_{O_2}^{sat}}$	Non-dimensional concentration in the electrolyte layer
$\theta_i^{init} = \frac{c_i^{init}}{c_{O_2}^{sat}}$	Non-dimensional initial concentration in the electrolyte layer
$d_i = \frac{D_i}{D_{O_2}}$	Non-dimensional diffusion coefficient of species
$\psi_i = d_i \frac{\partial \theta_i}{\partial \xi}$	Non-dimensional flux of species
$e_{corr} = \frac{F}{RT} E_{corr}$	Non-dimensional corrosion potential
$e^{0}_{Cu CuCl_{2}} = \frac{F}{RT} E^{0}_{Cu CuCl_{2}}$	Non-dimensional reduction potential of metal oxidation
$e_{O_2 OH^-}^0 = \frac{F}{RT} E_{O_2 OH^-}^0$	Non-dimensional reduction potential of oxygen reduction
$j_{corr} = \frac{i_{corr}}{i_{O_2 OH^-}^0}$	Non-dimensional corrosion current density

6.2.2.5. Solutions

Assume the diffusion processes in the electrolyte reach the pseudo-steady state at each time step. For each time step, diffusions of oxygen and chlorine ion are described below:

$$\frac{\partial^2 \theta_i(\xi, \tau)}{\partial \xi^2} = 0, \qquad (i = 1, 2)$$
(22)

where $1 = 0_2, 2 = Cl^-$.

For oxygen, boundary conditions are:

$$\xi = 0: \ \theta_{O_2}(0,\tau), \tag{23}$$

$$\xi = \frac{L}{L_0} : \theta_{O_2} \left(\frac{L}{L_0}, \tau \right) = \frac{c_{O_2}^{init}}{c_{O_2}^{sat}} = \frac{c_{O_2}^{sat}}{c_{O_2}^{sat}} = 1.$$
(24)

For chlorine ion, boundary conditions are:

$$\xi = 0: \ \theta_{Cl^{-}}(0,\tau), \tag{25}$$

$$\xi = \frac{L}{L_0}; \ \theta_{Cl^-} \left(\frac{L}{L_0}, \tau\right) = \frac{c_{Cl^-}^{init}}{c_{O_2}^{sat}} = \frac{9.17 \times 10^{-6}}{0.57}$$

$$= 1.61 \times 10^{-5}.$$
(26)

So, for oxygen, the solution is:

$$\theta_{O_2}(\xi,\tau) = \frac{L_0}{L} \Big(1 - \theta_{O_2}(0,\tau) \Big) \xi + \theta_{O_2}(0,\tau).$$
(27)

For chlorine ion, the solution is:

$$\theta_{Cl^{-}}(\xi,\tau) = \frac{L_0}{L} (1.61 \times 10^{-5} - \theta_{Cl^{-}}(0,\tau))\xi + \theta_{Cl^{-}}(0,\tau).$$
(28)

Then, substitute (27) and (28) into the equations (11) – (13) to obtain the formula of E_{corr} .

$$E_{corr} = -\frac{RT}{F} w lnA - \frac{2RT}{F} w ln(\theta_{Cl} - |_{\xi=0}) + \frac{RT}{F} w ln(\theta_{O_2}|_{\xi=0}) + (1 - w) E_{O_2|OH^-}^0$$
(29)
+ $w E_{Cu|CuCl_2}^0$,

where
$$A = \frac{10^4 L_0 F D_{CuCl_2^-}}{L} \frac{c_{O_2}^{sat^2}}{i_{O_2}^0}, w = \frac{1}{1 + \alpha_{O_2|OH^-}}.$$

Then substitute (27), (28) and (29) into non-dimensionalized (15) and (16):

$$1 - \theta_{O_2}(0,\tau) = \frac{L}{F D_{O_2} c_{O_2}^{sat}} i_{O_2|OH}^0 - A^{1-w} [\theta_{Cl^-}(0,\tau)]^{2(1-w)} [\theta_{O_2}(0,\tau)]^w \exp\left[\alpha_{O_2|OH^-} - w(e_{O_2|OH^-}^0 - e_{Cu|CuCl_2}^0)\right]$$
(30)

$$1.61 \times 10^{-5} - \theta_{Cl}(0,\tau) = \frac{10^4 D_{CuCl_2}}{D_{Cl}} c_{O_2}^{sat} A^{-w} [\theta_{Cl}(0,\tau)]^{2(1-w)} [\theta_{O_2}(0,\tau)]^w \exp[(1-w)(e_{O_2|OH^-}^0 (31) - e_{Cu|CuCl_2}^0)].$$

Combine (30) and (31) to calculate $\theta_{O_2}(0,\tau)$ and $\theta_{Cl}(0,\tau)$. Then, substitute these two values into (29) and (11) to get the E_{corr} and i_{corr} .

Then, solve the partial differential equation system (18) - (21). The analytical solution for the nondimensional species concentration at y = 0:

$$c_{i}(0,\tau) = c_{i}^{init} + \frac{i_{corr}}{FL}t + \sum_{n=1}^{\infty} \frac{2i_{corr}}{bn^{2}\pi^{2}F} \left(1 - e^{\frac{-bn^{2}\pi^{2}}{L^{2}}t}\right),$$

$$b = \frac{-i_{corr}}{D_{i}F}, \quad (i = 3, 4)$$
(32)

where $3 = CuCl_2^-$, $4 = OH^-$.

Next, i_{corr} is used at the oxide-copper interface to get the non-dimensional species (CuCl₂⁻ and OH⁻) concentration at y = 0 by equation (32). Finally, the molar ratio among CuCl₂⁻, OH⁻, and Cu₂O in 2CuCl₂⁻ + 2OH⁻ \rightarrow Cu₂O + H₂O + 4Cl⁻ is used to calculate the quantity of the generated Cu₂O.

6.2.3. Determination of Model Parameters

6.2.3.1. Parameters for chemical kinetics

 $i_{O_2|OH^-}^0$ – Kibria et. al. (Kibria & Tarafdar, 2002) studied the exchange current density for the oxygen evolution reaction (oxygen reduction reaction). In our model, the chemical reaction is a spontaneous reaction at the room temperature. So, the value of exchange current density was chosen under 300K and low overpotential. $i_{O_2|OH^-}^0 = 8.91 \times 10^{-3} A/m^2$.

 $\alpha_{O_2|OH^-}$ - King et. al. researched the copper corrosion by oxygen in neutral NaCl solution. This paper used 0.43 in 2% O₂+N₂ as the transfer coefficient of oxygen reduction. $\alpha_{O_2|OH^-} = 0.43$.

 $E_{O_2|OH^-}^0$ – The standard electrode potential for oxygen reduction is 0.401V (Popov, 2015). $E_{O_2|OH^-}^0 = 0.401V.$

 $E_{Cu|CuCl_{2}}^{0}$ – There was a study about measuring the standard reduction potential for copper dissolution in NaCl solutions under different temperatures (Bacarella, Griess, & Jr., 1973). $E_{Cu|CuCl_{2}}^{0}$ was -0.038V vs. SCE (Saturated Calomel Electrode) at 30°C and $\frac{dE_{Cu|CuCl_{2}}^{0}}{dT} = -0.4 \frac{mV}{deg}$. First, the $E_{Cu|CuCl_{2}}^{0}$ value vs. SCE was transferred to it vs. Standard Hydrogen Electrode (SHE). Then, $E_{Cu|CuCl_{2}}^{0}$ was calculated at 25°C vs. SHE. $E_{Cu|CuCl_{2}}^{0} = 0.204V$.

6.2.3.2. Parameters for diffusion coefficients

In our model, the chemical species diffuse through the porous Cu₂O layer. So, the diffusion coefficient was impacted by the porosity of copper oxide. Lots of researchers added coefficients to adjust the diffusion coefficient in the bulk solution. These coefficients described the characteristics of porous media and also quantitatively showed their effects on the molecular bulk diffusion coefficients. Figure 6-16 summarizes the history of studying the effectiveness of the diffusion coefficient through the metal oxide layer modeled as a porous media (Kantzas, Bryan, & Taheri).



Figure 6-16 History of Studying the Diffusion through the Porous Media (Kantzas, Bryan, & Taheri)

In order to simplify the calculation, our model ignored the surface diffusion and effect of the degree of saturation. Then we selected $D_e = \varepsilon_e \tau_t D$ to calculate the effective diffusion coefficients for the species. According to Moinuddin's research, the values of porosity ε_e and tortuosity τ_t of copper oxide were 0.205 and 0.05, respectively. But the degree of saturation is the important factor on atmospheric corrosion. So, it was accounted in the correction coefficient of current density for corrosion rate later. D_{O_2} – according to the Engineering Toolbox (Diffusion Coefficients of Gases in Water, 2008), we know that in the water under atmosphere pressure at 25°C, $D_{O_2} = 2.42 \times 10^{-9} m^2/s$.

 D_{OH^-} - Kallikragas et al. used the classical dynamics simulation to predict the diffusion coefficients for OH^- in water (Kallikragas, Plugatyr, & Svishchev, 2014). They showed the formulation of the diffusion coefficient was listed below:

$$D\rho = aT^{\alpha} + \rho(b_1T^{-2} + b_2T^{-1} + b_3 + b_4T)$$

+ $\rho^2 \ln \rho(c_1T^{-2} + c_2T^{-1} + c_3 + c_4T)$
+ $\rho^2(d_1T^{-2} + d_2T^{-1} + d_3 + d_4T),$ (33)

where a, α, b, c , and d are the fitting parameters, T is temperature in Kelvins, and ρ is the water density in g/cm³.

Table 6-2 Fitting Parameters of Equation (33) for the Diffusion Coefficients for OH Radical

Fit	OH radical
coefficients	
α	0.00408
а	1.38897
b_1	1.0

<i>b</i> ₂	-174613.7394
<i>b</i> ₃	847.03131
b_4	-0.71041
<i>c</i> ₁	1.0
<i>C</i> ₂	-153864.1999
<i>C</i> ₃	782.41564
<i>C</i> ₄	-0.64852
d_1	1.0
d_2	163191.6423
d_3	-795.71944
d_4	0.63849

So, we calculated the diffusion coefficient in Table 6-2 for OH radial at 25 °C. $D_{OH^-} = 2.7168 \times 10^{-9} m^2/s$.

 D_{Cl^-} - A study by Poisson and Papaud determined the diffusion coefficients of Cl⁻ in seawater (Poisson & Papaud, 1983). At 25°C, $D_{Cl^-} = 1.771 \times 10^{-9} m^2/s$. D_{cucl^-} - Diffusion coefficient of CuCl in aqueous solution at 298.15K is $1.297 \times 10^{-9} m^2/s$ (Ribeiro, et al., 2005). $D_{cucl^-} = 1.297 \times 10^{-9} m^2/s$.

6.2.3.3. Parameters for initial concentrations

$$c_{O_2}^{sat} - c_{O_2}^{sat} = 0.57 \frac{mol}{m^3}.$$

 c_{Cl^-} – First, $Cl_2(g)$ dissolve into the adsorbed moisture layer. This process is evaluated by Henry's law:

$$H^{cp} = \frac{c_a}{p},\tag{34}$$

where H^{cp} is the Henry's law constant, c_a is the concentration of a species in the aqueous phase (mol/l), p is the partial pressure of that species in the gas phase under equilibrium (atm).

At 25 °C, for $Cl_2(g)$, one part per billion (ppb) denotes one part in 10⁹. According to the literature, $H^{cp} = 9.2 \times 10^{-4} \ mol/(m^3 \cdot Pa)$. Our experiment condition shows that $p = 2ppb/10^9$. So, $c_a = c_{Cl_2} = 1.84 \times 10^{-12} \ mol/m^3$. Second, $Cl_2(g)$ reacts with the water and generates Cl^- , which is described by the following reaction:

$$Cl_{2(aq)} + H_2O \rightarrow H^+ + Cl^- + HOCl, \quad k = \frac{[H^+][Cl^-][HOCl]}{[Cl_{2(aq)}]} = \frac{[Cl^-]^3}{[Cl_{2(aq)}]} = 4.2 \times 10^{-4},$$

So, $c_{Cl^-}^{init} = 9.17 \times 10^{-6} \ mol/m^3$.

6.2.3.4. Parameter for initial thickness of the oxide layer on the copper

As we know, when the bare copper was exposed to the air, the direct oxide corrosion occurred on the surface and formed the initial oxide layer on the top of it. In this model, we use the regression results of normalized Chris' data (Muller, 1990) to predict the initial copper oxide thickness, which is shown in Figure 6-17. So, the regression shows that at the initial time the corrosion thickness is around 51 Angstroms. It is assumed that the initial copper oxide is constant ($L_0 = 51$ Angstroms) in this study since the copper specimens used were prepared in the same way as those used in Chris' study.


Figure 6-17 Regression for Modified Chris' Data under 25°C and 1.9 ppb Cl₂

A summary of parameters used in the model is provided in Table 6-3.

Table 6-3 Parameters U	sed in the Model
------------------------	------------------

Description	Parameter	Unit	Value
Exchange current density of the oxygen reduction reaction	i ⁰ _{02 0H} -	A/m ²	8.91 × 10 ⁻³
Transfer coefficient of oxygen reduction reaction	$\alpha_{O_2 OH}$ -	_	0.43
Standard reduction potential of oxygen reduction reaction	E ⁰ _{O2 OH} -	V	0.401

Standard reduction potential of copper dissolution reaction	$E^0_{Cu CuCl_2^-}$	V	0.204
Diffusion coefficient of dissolved oxygen in the water	D ₀₂	m²/s	2.42×10^{-9}
Diffusion coefficient of OH ⁻ in the water	D _{OH} -	m²/s	2.7168×10^{-9}
Diffusion coefficient of Cl ⁻ in the water	D _{Cl} -	m²/s	1.771×10^{-9}
Diffusion coefficient of CuCl ⁻ in the water	D _{cucl} -	m²/s	1.297×10^{-9}
Initial concentration of generated Cl ⁻	C_{Cl}^{init}	mol/m ³	9.17×10^{-6}
Initial concentration of dissolved oxygen	$C_{O_2}^{sat}$	mol/m ³	0.57
Porosity of copper oxide	ε _e	_	0.205
Tortuosity of copper oxide	$ au_t$	-	0.05
Initial copper oxide thickness	L ₀	Angstrom	51

6.2.4. Model Implementation

The model was implemented with MATLAB code as follows:

- 1) Input all the parameters and set initial dimensionless thickness to $\xi = \xi_0 at \tau = 0$.
- 2) Combine (31) and (32) to calculate the initial $\theta_{O_2}(\tau,\xi)$ and $\theta_{Cl}(\tau,\xi)$.
- 3) Substitute these initial conditions into Equation (11), (29), and (32), and obtain i_{corr} , θ_{CuCl} -(τ , ξ) and θ_{OH} -(τ , ξ) at the copper top surface.
- 4) Compare concentration of CuCl₂⁻ to concentration of OH⁻ and choose the lower concentration to calculate the generated concentration of Cu₂O by the 2:1 ratio between CuCl₂⁻ and Cu₂O based on the stoichiometry: (2CuCl₂⁻ + 2OH⁻ → Cu₂O + H₂O + 4Cl⁻). Transfer the concentration of Cu₂O to the thickness (Δξ) per second assuming the reaction occurs on the unit area (1 m²).
- 5) Add this generated thickness to ξ_{τ} for the next time step. Then by using the new $\xi = \xi_{\tau} + \Delta \xi$ to iterate through the steps 2), 3), 4) and 5).

This process is shown in Figure 6-18. This model was used to predict the corrosion development over the period used in the experiments.



Figure 6-18 Model Implementation

6.2.5. Model Verification

In order to verify the model, reference corrosion data for each thermal condition are needed but not available. To overcome this problem, we assumed that:

- Corrosion development under a pollutant mixture where Cl₂ has the dominating effect is similar to that under the exposure of a single pollutant Cl₂ in the air, and hence has the same relative change of corrosion thickness for a unit change in temperature or relative humidity.
- The corrosion thickness at day 6 can be used as the reference thickness. This assumption is adopted for practical reason since the majority of experiments conducted and reviewed contain the thickness measurements at day 6.
- 3) The growth rate of the corrosion thickness during a 6-day period is directly proportional to the current density generated from the copper dissolution reaction and oxygen reduction described by Equation (11) (13). Hence a correction coefficient, R, for the current density can be applied to Equation (11) (13) based on the ratio of day-6 corrosion thickness growth rate at the exposure condition of interest to that at the reference condition (25°C and 50% RH).

Based on the above assumptions, experimental data collected were "normalized" to the reference condition (25°C and 50% RH) using the following procedure:

Based on our experiment results with 6 days exposure under different pollutant mixture containing Cl_2 at 50%RH, the relative change of corrosion thickness for a unit change in temperature is 133.96 Angstroms for $O_3+NO_2+SO_2+Cl_2$ and 166 Angstroms for $O_3+NO_2+SO_2+Cl_2+H_2S$ in **Error!** Reference source not found.. Then it is used to normalize our experiment results for $O_3+NO_2+SO_2+Cl_2$ and $O_3+NO_2+SO_2+Cl_2+H_2S$ from 21°C and 25°C at 50% RH.

T (°C)	RH (%)	Pollut:	ants	Corrosion thickness (Angstrom)	R	elative change o osion thickness v increasing 1°C (Angstrom)	uf with	Relative change of corrosion thickness with increasing 4°C (Angstrom)
21	50	O3+NO2+5	SO ₂ +Cl ₂	1360.1		70 661		575 07
28	50	O3+NO2+5	SO ₂ +Cl ₂	422.4		06.001-		0.000-
21	50	O ₃ +NO ₂ +SO	2+Cl2+H2S	1505.4				
28	50	O3+NO2+SO	2+Cl2+H2S	343.4		-166		-004
	Use the r	elative change of	f corrosion thick	ness with increas	sing 4°C1	to normalize our	results 1	from 21°C to 25°C
RH (%)	Po	ollutants	Increment corrosion thic with increasin from 21°(Angstrom	of Corro kness thickn ug 4°C 21° C (Angst	osion ess at °C rom)	Normalized corrosion thickness at 25°C (Angstrom)	Ratio	= corrosion thickness at 25°C corrosion thickness at 21°C
50	O3+N(02+S02+Cl2	-535.83	136(0.1	824.27		0.61
50	O_3+NO_2 -	$+SO_2+Cl_2+H_2S$	-664	1505	5.4	841.4		0.56
	4	Mean ratio of cor	rrosion thickness	between 21°C ar	nd 25°C			0.58

Table 6-4 Calculation of Mean Ratio of Corrosion Thicknes

02+Cl2 +Cl2+H2S	Increment of corrosion thickness with increasing 4°C from 21°C (Angstrom) -535.83 -664 -664 sion thickness betwee	Corrosion thickness at 21°C (Angstrom) 1360.1 1505.4 1505.4 an 21°C and 25°C	Normalized corrosion thickness at 25°C (Angstrom) 824.27 841.4	Ratio = corrosion thickness corrosion thickness 0.61 0.56 0.58
	unts 02+Cl2 :+Cl2+H2S	Increment of corrosion thickness with increasing 4°C from 21°C (Angstrom) (O2+Cl2 -535.83 :+Cl2+H2S -664 -664	Increment of corrosion thickness with increasing 4°C from 21°C (Angstrom)Corrosion thickness at 21°C (Angstrom)iO2+Cl2-535.831360.1iO2+Cl2-535.831360.1i+Cl2+H2S-6641505.4i ratio of corrosion thickness between 21°C and 25°C	Increment of corrosion thickness with increasing 4°C from 21°C (Angstrom)Normalized corrosion 25°C (Angstrom)02+Cl2-535.831360.1824.27.02+Cl2-535.831360.1824.27.02+Cl2-535.831360.1824.27.02+Cl2-535.831360.1824.27.02+Cl2-535.831360.1824.27.02+Cl2-535.831360.1824.27.02+Cl2-535.831360.1824.27.1202-535.831505.4841.4.1212-6641505.4841.4.1210 of corrosion thickness between 21°C and 25°C1360.1

In Table 6-5, the mean ratio is used to convert the Chris' data (Muller, 1990) under 1.9 ppb Cl₂ only at 22°C to the modified data at 25°C.

Exposure time (day)	Chris' data at 22 ± 2°C	Mean ratio of corrosion thickness between 21°C and 25°C	Normalized Chris' data at 25°C
3	108	0.58	62.91
6	127	0.58	73.97

Table 6-5 Temperature Conversion (Cl₂ only under 50% RH)

Moreover, the normalized Chris' data for Cl_2 only at 25°C and 50%RH is the reference corrosion data. Its result of 73.97 Angstroms after exposing 6 days is taken as the reference to calculate the ratio among different pollutant mixtures under different thermal conditions in Table 6-6.

Table 6-6 Ratio among Different Pollutant Mixtures under Different Temperature

T (°C)	RH (%)	Pollutants	Corrosion thickness (Angstrom)	$Ratio = \frac{corrosion thickness(Ang.)}{73.97 (Ang.)}$
25	50%	O ₃ +NO ₂ +SO ₂ +Cl ₂	824.3	11.143
25	50%	$O_3+NO_2+SO_2+Cl_2+H_2S$	841.4	11.375
28	50%	O ₃ +NO ₂ +SO ₂ +Cl ₂	422.4	5.710
28	50%	$O_3+NO_2+SO_2+Cl_2+H_2S$	343.4	4.642

Chen, et al. (Chen, Zakipour, Persson, & Leygraf, 2004) studied the relative humidity effect on the copper corrosion under the Cl⁻ contaminant. Their results in Figure 6-19 were regressed by the equation $y = 7.8273 \ e^{3.8847x}$ (y = corrosion thickness - Angstrom), x = relative humidity - %).



Figure 6-19 Relative Humidity Effect on Copper – Corrosion Results after Exposure 10 Days under 2 µg/cm² Cl⁻ at 25°C (studied by Chen, et al.)

According to the equation, the results at different RH are given in Table 6-7. The corrosion thickness calculated at 25°C and 50%RH is as the reference to get the ratio among different relative humidity.

Table 6-7 Corrosion Results under Different Relative Humidities (Based on the RegressionRelationship of Study by Chen et. al)

T (°C)	RH (%)	Corrosion Thickness (Angstrom)	$Ratio = \frac{corrosion thickness(Ang.)}{54.60 (Ang.)}$
25	50%	54.6	-
25	75%	144.19	2.64
25	95%	313.59	5.74

So, based on the above data, it can be summarized to the change ratios among different thermal conditions by using the normalized corrosion thickness at 25°C and 50%RH with Cl_2 only as the 208

reference in Table 6-8. According to these ratios, the modified experimental data (normalized data) in Figure 6-20 were calculated and used to validate the corrosion model results.

T (°C)	RH (%)	Pollutants	Ratio = $\frac{\text{corrosion thickness}}{\text{corrosion thickness at 25°C and 50% Cl2 only}}$
25	50	Cl ₂	-
25	75	Cl ₂	2.64
25	95	Cl ₂	5.74
25	50	O ₃ +NO ₂ +SO ₂ +Cl ₂	11.143
25	50	O ₃ +NO ₂ +SO ₂ +Cl ₂ +H ₂ S	11.375
28	50	O ₃ +NO ₂ +SO ₂ +Cl ₂	5.71
28	50	O ₃ +NO ₂ +SO ₂ +Cl ₂ +H ₂ S	4.642

Table 6-8 Ratios of Corrosion Thickness under Different Exposure Conditions

Then in Table 6-9 the corrosion development can be calculated by the ratios listed in Table 6-8.

Table 6-9 Corrosion Development under Different Thermal Conditions

T (% C)	DH (%)	Dollutonto	Datia	Corrosion Thick	ness (Angstrom)
I (C)	KII (70)	ronutants	Natio	Exposed 3 days	Exposed 6 days
25	50	Cl_2	1	62.91	73.97
25	75	Cl_2	2.64	166.08	195.29
25	95	Cl_2	5.74	361.09	424.62
25	50	O_3 + NO_2 + SO_2 + Cl_2	11.143	700.98	824.3
25	50	O ₃ +NO ₂ +SO ₂ +Cl ₂ +H ₂ S	11.375	715.58	841.46
28	50	O_3 + NO_2 + SO_2 + Cl_2	5.71	359.2	422.4
28	50	O ₃ +NO ₂ +SO ₂ +Cl ₂ +H ₂ S	4.642	292.02	343.39

The model introduced one parameter - correction coefficient R - for current density generated by the chemical reaction (Equation 13). This coefficient is to calibrate and scale the current density

for our normalized experimental results. The copper oxide formed is porous, whose moisture adsorption affects the effective porosity for diffusing the chemical species through the electrolyte and for the concentration of species. For mixture compounds containing chloride, the coefficient R not only represents the chemical reaction barrier, but also the synergistic effect. According to our previous experiments, the dominant compound for copper corrosion is chloride. So, our model assumed the dominant chemical reaction is the same as the chloride only and the coefficient R was used to partially account for the synergistic effects empirically. The correction coefficient for current density, R, for different thermal conditions were calculated using MATLAB's fmincon function.



Corrosion Development under Different Conditions

Figure 6-20 Normalized Data and Linear Regression for Corrosion Development under Different Conditions after 6 Days Exposure Then it gives the corresponding correction coefficient R for each exposure condition in Table 6-10. It is noted that the correction coefficient has significantly higher values for the two test mixture conditions, $O_3+NO_2+SO_2+Cl_2$ and $O_3+NO_2+SO_2+Cl_2+H_2S$, compared to the Cl_2 alone condition. This is an indication that the correction coefficient has implicitly accounted for some synergistic effects of multi-compounds. The correction coefficient is in the order of 10^{-10} to 10^{-7} , indicating a significantly lower current density comparing to the theoretical values and those found in the previous studies in which there exist effects of porosity and electric field on corrosion development (Bortels, et. al., 1996; Venkatraman et.al, 2011; Larson, 2002). The exact reason is unknown and requires further investigation.

Т	RH (%)	Pollutants	Correction Coefficient R for Current Density $R \times i_{corr}$	Root-mean- square Error
25	50	Cl_2	$10^{-10.5629}$	0.9572
25	75	Cl_2	$10^{-9.0815}$	5.6928
25	95	Cl ₂	$10^{-8.0591}$	13.2073
25	50	O ₃ +NO ₂ +SO ₂ +Cl ₂	$10^{-7.1942}$	25.9251
25	50	O ₃ +NO ₂ +SO ₂ +Cl ₂ +H ₂ S	$10^{-7.1674}$	26.4648
28	50	O ₃ +NO ₂ +SO ₂ +Cl ₂	$10^{-8.0659}$	13.136
28	50	O ₃ +NO ₂ +SO ₂ +Cl ₂ +H ₂ S	$10^{-8.3369}$	10.5764

Table 6-10 Calculation for Correction Coefficients R of Current Density

6.3. Results and Discussion

6.3.1. Corrosion Thickness Development

Using the model and related parameters described in the previous section, the corrosion thickness over time is predicted as the reference case (25°C and 50% RH with Cl_2 only) shown in Figure 6-21 along with the normalized experimental data (modified data) that represent corrosion thickness after exposing 0 days, 3 days and 6 days, respectively.



Figure 6-21 Corrosion Development for Modified Data with Cl₂ only at 25°C and 50% RH (Reference Case)

At the beginning of copper corrosion, corrosion thickness increases in 6 days. The model R-meansquared error is 0.9572.

6.3.2. Effects of Relative Humidity

Figure 6-22 shows the predicted effects of relative humidity on the corrosion thickness development.



Figure 6-22 Effects of Relative Humidity – Corrosion Results under Different Relative Humidity with Cl₂ only at 25°C

The model correctly predicted the faster corrosion development under higher RH conditions. The fastest corrosion is for 95% relative humidity. For the species transport, higher relative humidity may improve the moisture adsorption for porous copper oxide, which will give a better effective porosity for species to move through the porous copper oxide. So, it may accelerate the generation of copper oxide. However, for the chemical reaction, higher relative humidity dilutes the concentration of each species, which may slow down the corrosion process. So, according to our

experiment and model results, it shows relative humidity is the dominant effect for the species transport.

6.3.3. Effects of Temperature

Based on our experimental data, we know it is helpful for us to prevent copper corrosion by increasing the temperature. In Figure 6-23 and Figure 6-24, for mixture pollutants containing chloride, when temperature increases from 25°C to 28°C, the rate (slope) of corrosion development is decreased. Increasing temperature causes the corrosion barrier, which slows down the corrosion process. From the point of view of chemical reaction, increasing temperature activates the reaction process, which means worse corrosion. But in our results, it shows an opposite corrosion trend. Corrosion with higher exposure temperature has a lower corrosion rate. Increasing temperature at the same relative humidity will decrease the moisture content on the copper surface and throughout the porous, which may be the limitation of species transport. So, it means temperature may have more influence on the moisture adsorption for diffusing species than on the chemical reaction rate.



Figure 6-24 Effects of Temperature with O3+NO2+SO2+Cl2 at 50% RH



Figure 6-23 Effects of Temperature with O3+NO2+SO2+ H2S +Cl2 at 50% RH

6.3.4. Effects of Multiple Pollutants

This model uses the case with Cl_2 only as the baseline, because our experiment results show chloride is the dominant compound for copper corrosion under mixture pollutants. As shown in Figure 6-25, compared to pollutant mixture containing chloride, chloride alone does not cause significant copper corrosion after 6 days of exposure, with a corrosion thickness of less than 100 Angstroms. But when chloride combines with $O_3+NO_2+SO_2$ or $O_3+NO_2+SO_2+H_2S$ at 25°C and 50% RH, it causes a sharp increase of corrosion thickness. Between mixture $O_3+NO_2+SO_2+Cl_2$ and mixture $O_3+NO_2+SO_2+H_2S+Cl_2$, there is no significant difference in corrosion thickness, which agrees with the normalized experimental data.



Figure 6-25 Effects of Multiple Pollutants at 25°C and 50% RH

6.3.5. Limitation of the Model

The kinetics of chemical reaction and mass transfer are considered in this model. But the synergistic effects of multiple pollutants on the chemical reactions have not been explicitly modeled though implicitly accounted for using the correction coefficient for the current density due to chemical reactions at the oxide-metal interface. Because our experimental results show that chloride is the dominant compound, copper corrosion due to chloride alone was used as the reference to predict the correction coefficients for the test mixtures investigated. As a result, the model also does not account for the effects of further reaction products. For longer immersion of copper under chloride-containing thin electrolyte layer, Cu_2O will continue to react with Cl⁻ and oxygen to generate a steadier corrosion product $Cu_2(OH)_3Cl$ to $Cu_2(OH)_2CO_3$ (Liao, et al., 2011). Such multi-stage reaction effects need to be considered in developing a more accurate prediction model.

The properties of the corrosion products are also the key to affect the species transport, moisture adsorption, and electronic conductivity. The present model accounted for the effect of reaction products' porosity on the diffusion coefficient in the bulk solution. But there is lack of knowledge on the effects of effective porosity under different thermal conditions (temperature and relative humidity) on the moisture adsorption, which can also have significant impact on the ion transport (such as ion mobility, diffusion coefficient of ion, and concentration of species).

The solution to the model assumes that the species transports reach the pseudo-steady state instantaneously at each time step. However, when the corrosion thickness becomes thicker, unsteady calculation for the mass transport would be necessary.

6.3.6. Future Work

In order to develop a more accurate prediction model for corrosion process, it is necessary to improve the understanding of the synergistic effects of pollutant mixture and thermal conditions. It includes the effects of pollutants concentration, pollutant mixture, relative humidity, temperature, exposure time, and properties of corrosion products on the corrosion mechanism and magnitudes. More kinetic reaction data under different thermal conditions are also needed to better estimate the model parameters related to the chemical reactions including exchange current density, transfer coefficient of reduction reaction, and standard reduction potential.

Another important need is to improve the understanding of actual field pollution and thermal condition in-situ (existing data are very limited) in conjunction with the field corrosion measurements by standard coupons. Comprehensive field-testing protocols should be developed to measure corrosion thickness, weight loss, corrosion products on the surface/cross-section of the sample along with the monitoring of the air temperature, relative humidity, and concentrations of target pollutants causing the corrosion. Such data are necessary for field validation of the corrosion mode as well as for understanding the corrosion characteristics under the field conditions.

6.4. Summary and Conclusions

Corrosion is a complex process and is affected by many factors including exposure thermal conditions (temperature and relative humidity), exposure time, properties of corrosion products (such as effective porosity, adsorption of moisture, density etc.), and chemical reactions. According to our experiments and model, these factors interact with each other. Temperature and relative humidity have an impact not only on the moisture adsorption of porous copper oxide, but also on the corrosion rate (current density). With time, corrosion mechanism will change because of the generation of corrosion product layer. For our concentration levels, it is important for us to further study the characteristics of porous products and how thermal condition affects them. For the synergistic effects, there is still a lack of knowledge of corrosion mechanism and corresponding kinetic parameters data.

A mechanistic model has been developed to predict the corrosion thickness overtime on copper due to exposure to chloride-containing mixture, accounting for the effects of humidity and temperature. In this model, the corrosion system is represented by the bare copper, the oxide layer on the copper surface consisting of the initial copper-oxide layer, its subsequent development due to corrosion, and the adsorbed water, and the air-boundary layer over the oxide surface. The corrosion is modeled as an electro-chemical process in which the adsorbed moisture of the oxide layer is the electrolyte in which the ions dissolved from air-boundary layer migrate toward the oxide-copper interface and the ions of chemical species released from the copper surface dissolve into the electrolyte and migrate toward the oxide-air interface. The model accounts for the transfer of electrons in copper, the metal oxidization/dissolution and oxygen reduction at the copper-oxide interface, diffusion of ions in the adsorbed water-containing oxide layer, the dissolution of oxygen, and the dissolution and reduction of chloride gases at the oxide-air interface.

Model parameters were first estimated based on the data available from the literature. In order to apply the model to predict the corrosion development under the conditions of experiments conducted in the present study, a correction coefficient for the current density generated from the oxidization/reduction was proposed and estimated by using the normalized measurement data. The model was then applied to predict the growth of the corrosion thickness and the effects of air temperature and relative humidity. Results show that the model is capable of accurately predicting the corrosion thickness development over time, less corrosion at a higher air temperature, and more corrosion at a higher relative humidity as observed in the experiments where chloride was identified as the dominant pollutant for corrosion. Further research is needed both experimentally and theoretically to account for the synergistic effects of multi-pollutants in the corrosion development when no single pollutant is dominating the process.

7. Conclusions and Recommended Future Studies

In order to reduce energy consumption in data centers by using free cooling outdoors, it is vital to understand how different gaseous pollution in the air impact the reliability of IT equipment under different thermal conditions. An experimental and modeling study has been conducted on the corrosions of copper and silver; the two common materials used in IT equipment. The following conclusion can be drawn from the present study:

- 1) Effects of thermal environmental conditions:
- a) Relative humidity: For copper, increasing relative humidity caused more severe corrosion. But for silver, it did not have a significant influence on the corrosion thickness for all pollutant mixtures tested except for the five-compound mixture. For copper, the results show that a critical relative humidity exists between 70% and 80%, above which corrosion would sharply increase regardless of the pollutant mixtures. So, for data center environments the relative humidity should not be above 70% at 21°C for copper and silver corrosion control.
- b) Temperature: For copper, higher temperature dramatically reduced corrosion thickness. However, for silver, significant corrosion thickness was still detected with pollutant mixtures containing H₂S. The change of temperature did not cause the fluctuation of corrosion development. For data center environments where Cl₂ and H₂S are not present, temperature can reach 28°C for corrosion control when relative humidity is at or below 50%.
- c) Relative humidity fluctuation: for copper, when 10% RH fluctuation was added to the test conditions at 21°C and 50% RH with five pollutant compounds and at 21°C and 80% RH with O₃, NO₂, and SO₂, it caused obviously worse corrosion compared to the tests without relative humidity fluctuation. However, the RH fluctuation did not cause a significant change in corrosion. Considering both copper and silver, the range of RH fluctuation in data centers should be controlled.
- 2) Effects of Pollutant Mixture: Copper corrosion is severe with all Cl₂-containing pollutant mixtures, and synergistic effects were pronounced between Cl₂ and other co-existing compounds including O₃, NO₂, SO₂, and H₂S. But for the silver, the dominant compound was H₂S. Both Cl₂ and H₂S should be strictly limited in data centers. For data centers where only

the pervasive compounds (O₃, NO₂, and SO₂) exist in the air and standard field coupon tests show less than 200 Angstroms and 300 Angstroms over a 30-day period, the thermal envelope for environmental design can be extended to a higher relative humidity (up to 70% RH) and a higher temperature (up to 28°C).

3) A mechanics corrosion model was developed to predict the corrosion development for copper over time. There are three main layers involved in this model: gas layer, copper oxide layer containing adsorbed water (electrolyte), bare copper layer. Electrochemical reaction occurs at the oxide-copper interface. Chemical species (oxygen and ions) diffuse through the porous copper oxide layer in the electrolyte and electron migration presents in the bare copper. In this model, the correction coefficient for current density is introduced to calibrate the normalized experimental data. The model's prediction on the corrosion thickness development and effects of T and RH are consistent with those found in the experiments.

Further studies are needed in the following areas to better understand the ITE failure due to atmospheric corrosion:

- Synergistic effects of multiple pollutants on the corrosion of copper and silver subjecting to different temperature and humidity conditions and the associated electro-chemical, heat and mass transfer, and thermodynamic processes.
- 2) Mechanistic consideration of the synergistic effect in the prediction model and validation of the model for a longer period of time (e.g., over 30 days for comparison with the standard field monitoring results as well as laboratory data).

- Correlation between the laboratory testing results and the corrosion development under actual field conditions.
- Development of an accelerated laboratory test method to determine the model parameters, which would enable the prediction of the reliability and service life of IT equipment in data center environment.

8. Implications for Environmental Control in Data Centers

In this section, we first review the basis for testing the corrosion effects for the data center environment, and make some recommendations based on the test results and analysis from the present study.

8.1. Basis for recommendations

Since both silver and copper are materials used in all electronics applications, any recommendations for changes to the ASHRAE recommended envelope has to take into account the worst-case results from the tests of both silver and copper. From a review of both stacked bar charts for copper and silver in Chapter 5, it appears that the results with the copper coupon will be controlling any changes made to the recommended environmental envelope of data center.

It is also assumed that the currently recommended envelope is suitable for ensuring acceptable reliability of the IT equipment based on the field experience where the corrosion thickness does not exceed 200 Å/month and 300 Å/month for copper and silver, respectively. Since the actual

pollutant mixture condition and concentration levels are not known from the field cases from which the criteria were derived, it is not possible to correlate the laboratory corrosion thickness results to the field data directly as Abbott (1988) also pointed out. As a result, we assume that the corrosion levels at a reference condition (21°C and 50% RH) within the recommended thermal envelope are acceptable to be used as a reference, and any significant increase of corrosion from this reference level due to the increase of temperature or relative humidity would be deemed unacceptable for expanding the currently recommended thermal envelope. In other words, the recommended thermal envelope in the future can be expanded to the experimental relative humidity or temperature conditions where corrosion did not increase significantly from that measured at the reference condition (21°C and 50% RH).

8.2. Recommendations

 Since the currently recommended envelope for maximum moisture levels is set at a maximum of 60% RH for a range of temperatures from 18°C to 23°C and 15°C dew point between 23°C and 27°C, the previous results from these test conditions will be the basis for the following two recommendation:

21°C and 50% RH

28 °C and 50% RH

21 °C and 70% RH

- a) Copper stacked bar chart Test results show low levels of corrosion, and probably at levels that are acceptable no significant increase from the reference condition.
- b) Silver stacked bar chart Test results show low levels of corrosion, and probably at levels that are acceptable – no significant increase from the reference condition.

Recommendation: For data center environments tested with silver and copper coupons and shown to be of low levels of corrosion (less than 300 Å/mon for copper and 200 Å/mon for silver), suggesting that only pervasive pollutants may be present, then the moisture limit could be raised to 70% RH for temperatures between 18°C and 21°C. If the dew point limit could be relaxed to 17°C, then the temperature limit could be extended from 21°C to 22.5°C at 70% RH (thermal conditions inside the dashed envelope in Figure 8-1).



Figure 8-1 Possible Expansion of the Recommended Thermal Envelope for Data Centers Where Cl₂ and H₂S are not Present (as represented by the dashed envelope) (ASHRAE, 2015)

For the test results that included Cl_2 and H_2S (in combinations with NO₂, SO₂, and O₃) which are usually more localized pollutants as a result of some local natural event or manufacturing process:

- a) Copper stacked bar chart test results for 50% RH and 70 % RH at 21 °C are quite corrosive environments as evidenced by the height of the bars.
- b) Silver stacked bar chart test results for 50% RH and 70% RH at 21 °C are quite corrosive environments for combinations where H₂S was present.

Recommendation: For data center environments tested with silver and copper coupons and shown to be of high levels of corrosion (greater than 300 Å/mon for copper and 200 Å/mon for silver), suggesting that Cl_2 and/or H_2S (or other corrosive catalysts) may be present, then moisture levels should be kept lower than 60% RH levels and even lower than 50%RH if possible, given the very corrosive nature of these catalysts.

2) The review of the test results at 21°C and 80% RH compared to 21°C and 70% RH is shown below:

For the test results from only the pervasive gases of NO₂, SO₂, and O₃:

- a) Copper stacked bar chart test results at 21°C and 80% were quite corrosive for all gaseous pollutants combinations. However, test results at 21°C and 70% for the pervasive gases of NO₂, SO₂, and O₃ in any combination were quite low, suggesting that a relative humidity change from 70% to 80% caused a significant increase in corrosion.
- b) Silver stacked bar chart test results at 21°C and 80% were quite low for all gaseous pollutant combinations. Similar results were obtained for 21°C and 70%.

Recommendation: Given the increase in corrosion for copper at 80%, the RH level should not exceed 70 % at 21°C.

3) Materials:

The relative magnitudes of the silver and copper corrosion depending on temperature, humidity, and pollutants should be noted. One is that copper at higher temperature (28°C) was notably at some of the lowest corrosion levels for all pollutant combinations.

Recommendation: As the air increases in temperature moving from front to back of a server that it might be beneficial to reducing the effects of copper corrosion by placing copper containing components at the rear of the server where the temperature is higher, especially when catalyst type pollutants exist.

The coulometric reduction results for copper and all pollutant levels definitely suggest that higher temperatures result in less corrosion.

Recommendation: Using copper materials predominately in the rear of the server is acceptable.

However, the use of silver in the manufacturing process for servers for components located anywhere in the server (front, back, or anywhere in between) could be fine for all pollutants tested except when H_2S exists. When H_2S exists as one of the pollutants, any components that employ silver and for components located in any location in the server, detrimental levels of corrosion can occur.

4) Data center operators:

Recommendation: At least twice a year (once in the winter and once in the summer) data center operators should use silver and copper coupons to detect the level of corrosion. If results from both sets of test show levels below 300 Å /200 Å then it would be a good assumption that only the pervasive pollutants are present and there are no catalysts like H_2S or Cl_2 . The recommendations above should be followed as stated for servers manufactured of silver/copper. If coupon measurements are much higher than 300 Å /200 Å then it is a good assumption that highly corrosive catalysts like H_2S and/or Cl_2 exist and result in high levels of corrosion. The recommendations above should be followed as stated for servers manufactured with silver/copper. In addition, data center operators should take action to remove the highly corrosive catalysts type pollutants using chemical filtration.

5) Selection of site locations for new data centers

Recommendation: Selection of site locations for new data centers should include extensive coupon testing in and around the area to determine the possibility of high levels of corrosive pollutants. If there are buildings near the site of interest, then coupons should be placed in the buildings for a month to determine the level of corrosion. 6) Color index:

Recommendation: The color index (i.e., the relative RGB values) of the standard copper coupon surface when exposed in the data center environment can be used as a screening tool to estimate if the corrosion conditions is low (<500 Å) or severe (>1000 Å), and hence further actions are needed to confirm the pollution or corrosion levels and to improve the thermal environmental conditions and indoor air quality in accordance with the recommendations above.

9. Appendix

9.1. Appendix 1 - Test Procedure

For each test, the following procedure was followed:

- Check environmental parameters: flow meters, RH, and T, and record the values;
- Turn on the dynacalibrator and turn the status from "Vent" to "Span", check the flow rate for channel #2 (one of the two channels used for the present study);
- Turn on the ozone UV light and the ozone monitor. Then insert the measurement tube into the chamber #6. They need 0.5 hours to warm up.
- Turn the status to "Vent". Insert 4 permeation tubes into the dynacalibrator, close the cap tightly. Then turn on the heater (pushing the button) and set the temperature to 30 °C. Finally turn on the "Span";
 Note: The dynacalibrator needs at least 2 hours to warm up to achieve stable generation

rates.

- Prepare specimens and fill out the coupon labels. Then record the coupon number, tracking number, corresponding chamber number, and date;
- Hang all specimens inside the chamber, and record this time as Time Zero-i.e., start of the exposure time.
- Daily check RH (water level for the water tank), temperature, and flow. When the water level is lower than the marker, add some water. Record the adding date;
- At the 6th day after Time Zero (or another pre-specified exposure time), take out the coupons. Put them back in the package. Record the date.
- At the end of the test, turn on the "Vent" and turn off the heater for the dynacalibrator. Turn off the ozone generator;
- After 3-4 hours, after the temperature decreases to 21°C, turn off the power to the dynacalibrator; Then turn off the mass flow controller for the flow to the ozone generator;
- Download the temperature and relative humidity data from the data logger.

		10		C 1	<u> </u>	6	~	100				1.0								<u>~</u>			-	10		C 1	~			~		10	6	~		6	<u> </u>				~
Ag-Unk		3506	0	1502	1252	686	1753	526	451	270	421	275	351	0		1077	901	1402	4007	1753	1502	751	751	876	0	1002	1753	510	429	188	322	126	509	268	0	5		617	537	537	403
Ag2S		12218	11782	11345	11564	12436	11782	10473	10996	10813	10473	12480	11695	262	218	8138	6358	12218	7855	7200	6982	7418	7200	655	0	8727	7200	281	117	304	164	246	187	224	711	13		561	444	234	351
AgCI		677	677	677	677	761	677	609	609	650	893	711	745	0	0	0	0	812	0	0	677	677	338	0	0	0	0	0	0	0	0	0	0	0	0	0		254	145	0	0
Silver	30-day	16401	12459	13524	13493	14136	14212	11608	12056	11733	11787	13466	12791	262	218	9215	7259	14432	11862	8953	9161	8846	8289	1531	0	9729	8953	791	546	492	486	372	509	492	711	22		1432	1126	771	754
Silver	Actuak (calc.)	1640.1	1245.9	2704.8	2698.6	5654.4	5684.8	7738.666667	8037.333333	9777.5	9822.5	13466	12791	262	218	1843	1451.8	1443.2	1186.2	1790.6	1832.2	3538.4	3315.6	612.4	0	1945.8	1790.6	353.7	244.2	220.0	217.3	166.4	227.6	220.0	318.0	36.8		286.4	225.2	344.8	337.2
Silver	Class	1	1	1	1	1	1	1	1	1	1	1	1	0.5	0.5	1	1	1	1	1	1	1	1	0.5	0.3	1	1	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.3		1	1	0.5	0.5
Cu-Unk		10116	800	3793	4552	8093	5311	5538	5918	7405	7041	5817	5058	0	0	4552	14090	6575	14668	15679	14921	13403	14668	0	0	0	7587	0	18	485	0	0	0	121	1200	40		6667	4581	0	0
Cu2O		5489	1832	2745	3964	2707	2897	1830	1670	1043	1317	610	732	305	290	5794	2614	12808	3660	2135	2440	1982	4422	1350	0	0	2135	151	123	205	168	173	672	224	197	52		1046	1307	363	335
Cu2S		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	20000	0	0	0	0	0	0	0	0	0	0		0	0	0	0
Copper	30-day	15605	2632	6538	8516	10800	8208	7368	7588	8448	8358	6427	5790	305	290	10346	16704	19383	18328	17814	17361	15385	19090	1350	0	20000	9722	151	141	069	168	173	672	345	1397	92		7713	5888	363	335
Copper	Actual (calc.)	1560.5	263.2	1307.6	1703.2	4320	3283.2	4912	5058.6667	7040	6965	6427	5790	305	290	2069.2	3340.8	1938.3	1832.8	3562.8	3472.2	6154	7636	540	0	4000	1944.4	93.2	87.0	308.6	103.7	106.7	300.5	154.3	279.4	154.0		1542.6	1177.6	162.3	149.8
Copper	Class	1	1	1	1	1	1	1	1	1	1	1	1	0.3	0.3	1	1	1	1	1	1	1	1	1	0.3	1	1	0.3	0.3	0.5	0.3	0.3	0.5	0.5	1	0.3		1	1	0.5	0.5
Days in	Service	3	33	9	9	12	12	20	20	25	25	30	30	30	30	9	9	e	m	9	9	12	12	12	12	9	9	9	9	9	9	9	9	9	9	167		9	9	9	9
Chamber	No	4	4	2	2	3	3	4	4	2	2	5	5	7(referenci	7(referenci	2	2	1	1	2	2	5	5	7(referenci	7(referenci	3	3	7	7	3	3	7	7	3	3	8		4	4	7	7
CCC Panel	No.	113223	113151	113190	113193	113225	113187	113124	113142	113136	113203	113139	113211	113123	113171	113163	113162	113209	113215	113234	113143	113146	113217	113132	113150	113147	113148	113140	113160	113164	113129	113230	113206	113172	113159	113232	113161	113218	113153	113202	113189
Exposure condition			1			1	1		21C 50%KH five pollutants	1	1	1	1	1	1		- 21C 20%KH TOUR POILUTENTS (WITHOUT US)		1	1			1	1			21C 70%RH four pollutants (without O3)		TIC FOWBH Only On-		1				L				71/C EOW BH (02 : 502 : NO2 : CI2		

9.2. Appendix 2 – Data of Coulometric Reduction Analysis

						-		I							
	113170	4	9	1	1753.2	8766	0	1177	758	9	221.0	5 1108	109	409	590
	113224	4	9	1	1784.2	8921	0	654	826	7	214.0	5 1073	156	327	590
	113233	7	9	0.5	85.0	190	0	190		0	109.8	3 549	0	468	81
	113169	7	9	0.5	177.5	397	0	397		0 0.5	364.(0 814	0	304	510
	113195	4	9	1	318.0	1590	0	438	115	2 1	1148.6	5 5743	0	4723	1020
	113156	4	9	1	363.4	1817	0	775	104	2 1	1401.(7005	167	6033	805
21C 20%KH 03+202+N02+H22	113180	7	9	0.5	328.7	735	0	402	33	3 1	288.(5 1443	0	772	671
	113176	7	9	0.5	350.2	783	0	395	38	8	204.	1022	0	351	671
	113198	4	9	1	2011.2	10056	0	719	633	7 1	207.4	1037	73	374	590
	113182	4	9	0.5	225.8	505	0	134	37	1 0.5	248.2	2555	0	421	134
21C 66%KH U3+5U2+NU2	113201	7	9	0.5	305.9	684	0	193	49	1 1	201.6	5 1008	0	444	564
	113192	7	9	0.5	174.4	390	0	112	27	8	293.4	4 1467	0	608	859
	113126	с	9	0.5	222.7	498	0	313	18	5 0.5	225.8	3 505	0	210	295
	113207	ε	9	1	1430.0	7150	0	1634	551	6 0.5	442.	2066 7	0	561	429
21C SU%KH U3+NU2	113183	7	9	0.5	439.2	982	0	570	41	2 0.5	221.8	3 496	0	281	215
	113173	7	9	0.5	220.5	493	0	335	15	8 0.5	275.9	9 617	0	182	435
	113205	m	9	1	342.8	1714	170	877	99	7 1	293.4	4 1467	0	968	499
	113216	ε	9	1	293.6	1468	0	935	53	3 1	200.3	2 1001	0	486	515
	113226	7	9	0.5	380.6	851	0	336	51	5 0.5	338.3	1 756	0	327	429
	113222	7	9	0.5	189.6	424	0	424		0 0.5	337.	2 754	0	351	403
	113235	m	9	1	1294.8	6474	0	931	554	3 1	277.	4 1387	145	678	564
	113166	ю	9	1	358.8	1794	0	303	149	1 0.5	362.3	2 810	0	327	483
	113213	4	9	1	339.4	1697	0	224	147	3 1	211.3	2 1056	178	449	429
21C 50%RH O3+NO2 (Redupicated)	113219	4	9	1	403.2	2016	0	943	107	3 1	305.8	3 1529	87	433	1009
	113154	9	9	1	409.6	2048	0	248	180	0	260.3	2 1301	156	702	443
	113177	7	9	0.5	160.1	358	0	358		0 0.5	431.	1 964	0	374	590
	113220	7	9	0.5	169.0	378	0	123	25	5 0.5	286.2	2 640	0	117	523
	123633	3	9	1	238.2	1191	0	343	84	8	301.2	2 1506	0	1506	0
	123672	3	9	0.5	347.5	<i>LTT</i>	0	219	26	8 0.5	409.6	5 916	0	433	483
	123678	4	9	1	229.6	1148	0	227	26	1 0.5	413.	7 925	0	925	0
28C 50%RH O3	123683	4	9	0.5	335.4	750	0	132	61	8 1	223.8	3 1119	232	468	419
	123637	9	9	0.5	407.0	910	0	146	9/	4 1	374.2	2 1871	0	1871	0
	123675	7	9	0.5	424.4	949	0	343	09	6 1	203.(1015	0	398	617
	123682	7	9	0.5	338.1	756	0	241	51	5 1	304.(0 1520	0	1520	0
	123640	3	9	1	229.2	1146	0	219	26	7 0.5	398.	5 891	0	327	564
	123673	3	9	1	228.8	1144	0	247	68	7 0.5	446.3	866 8	0	448	550
	123665	4	9	0.5	424.9	950	0	162	9/	8 0.5	440.	586 5	0	416	542
28C 50%RH 03+S02	123671	4	9	0.5	437.4	978	0	117	98	1 0.5	424.9	950	73	421	456
	123687	9	9	1	203.2	1016	0	168	84	8 1	201.(0 1005	0	468	537
	123647	7	9	0.5	386.4	864	0	197	99	7 0.5	3.905	9 693	0	210	483
	123649	7	9	0.5	434.2	971	0	132	83	9 0.5	347.0	0 776	0	239	537

	123669	3	9	1	384.8	1924	0	263	1661	1	239.8	1199	272	468	459
<u>.</u>	123670	æ	9	0.5	445.4	966	0	190	776	0.5	334.5	748	0	748	0
	123642	4	9	1	1088.8	5444	0	2435	3006	0.5	435.1	973	58	421	494
28C 50%RH 03+NO2	123635	4	9	1	1046.2	5231	0	637	4594	1	227.8	1139	167	398	574
	123638	9	9	1	325.6	1628	0	234	1394	0.5	405.6	907	0	206	0
	123634	7	9	1	252.4	1262	0	256	1006	1	226.2	1131	0	514	617
	123680	7	9	0.5	328.3	734	0	110	624	1	255.0	1275	0	631	644
	113228	3	9	1	335.4	1677	0	229	1448	1	266.6	1333	0	1333	0
	123639	e	9	1	447.4	2237	0	146	2091	1	201.0	1005	0	468	537
	113200	4	9	0.5	390.4	873	0	497	376	0.5	303.2	678	0	678	0
28C 50%RH 03+N02+S02	123668	4	9	1	261.0	1305	0	190	1115	1	265.8	1329	526	374	429
	123679	9	9	1	303.0	1515	0	424	1001	0.5	376.6	842	0	842	0
	123659	7	9	0.5	416.4	931	0	234	69	0.5	418.1	935	0	935	0
	123674	7	9	0.5	361.3	808	0	190	618	0.5	364.9	816	0	285	531
	123656	Э	9	1	414.8	2074	0	292	1782	0.5	280.9	628	0	199	429
	123666	m	9	1	439.8	2199	0	248	1951	1	221.6	1108	345	374	389
	123641	4	9	1	1117.6	5588	0	2647	2941	1	291.8	1459	508	468	483
28C 50%RH 03+N02+S02+Cl2	123645	4	9	1	405.6	2028	0	380	1648	1	212.0	1060	145	351	564
	123686	9	9	1	429.4	2147	0	438	1709	1	285.0	1425	149	444	832
	123652	7	9	0.5	228.5	511	0	168	343	0.5	334.5	748	0	748	0
•	123663	7	9	0.5	345.7	773	0	181	612	0.5	390.0	872	0	872	0
	123653	£	9	1	371.0	1855	0	219	1636	1	855.6	4278	229	3601	448
	123664	£	9	1	206.8	1034	0	307	727	1	1047.2	5236	326	4373	537
	123643	4	9	1	293.2	1466	0	205	1261	1	1241.6	6208	65	5472	671
28C 50%RH 03+N02+S02+H2S	123644	4	9	1	352.0	1760	0	227	1533	1	1128.6	5643	131	4723	789
	123662	9	9	1	351.8	1759	0	292	1467	1	1510.4	7552	0	8033	1519
	123651	7	9	0.5	392.2	877	0	168	60/	1	258.6	1293	0	1293	0
	123661	7	9	1	218.4	1092	0	268	824	0.5	309.5	692	0	692	0
	123655	3	9	1	226.0	1130	0	88	1042	1	873.6	4368	580	2876	912
	123887	3	9	1	407.8	2039	0	263	1776	1	1184.2	5921	490	4747	684
	123906	4	6	1	368.8	1844	0	402	1442	1	1319.0	6595	399	5659	537
28C 50%RH 03+N02+S02+H2S+Cl2	123909	4	6	1	1161.6	5808	0	523	5285	1	1535.8	7679	508	6688	483
	123899	6	6	1	372.8	1864	0	234	1630	1	920.2	4601	363	3648	590
	123922	7	6	0.5	342.6	766	0	281	485	0.5	354.6	793	0	444	349
	123897	7	9	0.5	204.8	458	0	110	348	0.5	309.9	693	0	229	464
	123863	5	6	1	1579.8	7899	0	1177	6722	1	961.2	4806	363	4443	0
	123828	5	9	1	2137.0	10685	0	1307	9378	1	2171.8	10859	290	10569	0
28C->21C 50%RH 03+N02+S02+H2S+Cl2	123875	9	6	1	1812.4	9062	0	1961	7101	1	4000.0	20000	0	20000	0
	123879	7	6	1	205.0	1025	0	322	703	0.5	334.5	748	0	748	0
	123864	7	9	1	207.0	1035	0	380	655	0.5	292.9	655	0	655	0
	123878	3	<u>و</u>	1	2965.0	14825	0	2222	12603	1	2951.0	14755	725	14030	0
28C->21C 50%RH 03+N02+S02+H2S+Cl2	123869	4	ē	1	2454.6	12273	0	2033	10240	1	2587.4	12937	871	12066	0
	123865	3	9	1	3300.4	16502	0	1405	15097	1	2389.8	11949	725	11224	0

	123848	9	9	1	343.2	1716	0	322	139/	1	1067.6	5338	544	4794	0
<u>28C</u> ->21C <u>50%KH</u> 03+N02+S02+H2S+Cl2	123851	2	9	0.5	193.6	433	0	224	205	0.5	444.5	994	0	994	0
	123914	Э	9	0.5	583.6	1305	0	438	867	0.5	355.5	795	0	795	0
	123901	e	9	1	201.8	1009	0	512	497	0.5	407.9	912	0	912	0
	123907	4	9	1	256.4	1282	0	267	101	0.5	313.9	702	0	702	0
21C 80%RH O3	123908	4	9	0.5	398.9	892	0	650	242	1	561.2	2806	0	2086	0
	123915	9	9	0.5	228.5	511	0	358	156	0.5	136.0	304	0	304	0
	123913	7	9	1	4000.0	20000	20000	0		0.5	386.8	865	0	865	0
	123910	7	9	1	4000.0	20000	20000	0	0	1	271.2	1356	0	1356	0
	123900	æ	9	1	1020.8	5104	0	686	4418	1	519.6	2598	73	2525	0
	123918	ŝ	9	1	1041.8	5209	0	961	4228	1	272.8	1364	87	1277	0
	123885	4	9	1	416.4	2082	0	300	1782	1	205.8	1029	0	1029	0
21C 80%RH O3+NO2	123916	4	9	1	404.8	2024	0	563	1461	0.5	353.3	790	36	351	403
	123911	9	9	1	381.6	1908	0	314	159/	1 0.5	307.2	687	0	687	0
	123905	7	9	0.3	164.7	267	0	151	11(6.5	313.9	702	0	702	0
	123931	7	9	0.5	142.7	319	0	108	211	0.5	246.9	552	0	552	0
	123903	e	9	1	1608.6	8043	0	2419	5624	н т	219.0	1095	319	776	0
	123889	£	9	1	3780.8	18904	0	1503	1740	0.5	377.4	844	203	641	0
	123890	4	9	1	394.0	1970	0	734	1236	1	227.6	1138	109	1029	0
21C 80%RH 03+SO2	123883	4	9	1	256.8	1284	0	263	1021	1	286.2	1431	355	1076	0
	123929	9	9	1	3177.8	15889	0	1307	14582	0.5	405.6	206	51	856	0
	123892	7	9	0.5	191.9	429	0	227	202		261.8	1309	0	1309	0
	123898	7	9	0.5	219.1	490	0	212	278	0.5	418.1	935	0	935	0
	123925	e	9	0.5	894.4	2000	2000	0		0.5	379.7	849	218	631	0
	123886	æ	9	1	1831.4	9157	0	294	886	1	287.2	1436	337	1099	0
31/C 80% BH C2 - 5C3 - NO2	123896	4	9	1	314.2	1571	0	438	1133	1	203.6	1018	363	655	0
	123928	9	9	1	4000.0	20000	20000	0)	1	303.8	1519	326	1193	0
	123926	7	9	0.5	342.1	765	0	183	582	0.5	402.5	006	0	906	0
	123933	7	6	0.5	405.2	906	0	482	424	0.5	418.1	935	0	935	0
	123935	3	9	1	4000.0	20000	20000	0)	1	968.0	4840	0	4840	0
	123893	3	9	1	4000.0	20000	20000	0)	1	1150.8	5754	399	5355	0
	123920	4	6	1	4000.0	20000	20000	0)	1	1062.2	5311	73	5238	0
21C 80%RH 03+S02+N02+H2S	123895	4	6	1	4000.0	20000	20000	0)	1	1019.6	5098	0	5098	0
	123882	6	6	1	4000.0	20000	20000	0	0	1	1047.6	5238	0	5238	0
	123888	7	9	0.5	187.4	419	0	224	195	0.5	313.9	702	0	702	0
	123934	7	9	0.5	147.6	330	0	145	185	0.5	209.3	468	0	468	0
	123827	3	6	1	4000.0	20000	20000	0	0	1	203.6	1018	232	786	0
	123829	3	6	1	2909.2	14546	0	1536	13010	1	273.6	1368	363	1005	0
	123842	4	6	1	2133.8	10669	0	2042	8267	1 1	208.6	1043	435	608	0
21C 80%RH 03+SO+NO2+Cl2	123924	4	6	1	2279.6	11398	0	1912	948(6 1	218.0	1090	435	655	0
	123826	6	6	1	1764.6	8823	0	556	8267	0.5	339.0	758	127	631	0
	123917	7	6	0.5	145.3	325	0	246	25	0.5	209.3	468	0	468	0
	123843	7	9	0.5	136.4	305	0	184	121	0.5	157.0	351	0	351	0

0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
4653	7296	4536	6080	6734	5635	5752	7249	4920	4443	4443	6267	585	1964	608	1076	889	795	1403	678	1866	6734	6847	6678	6976	1740	685
435	290	580	363	435	399	0	374	348	363	399	435	0	0	508	508	218	363	725	0	0	0	0	0	496	0	0
5088	7586	5116	6443	7169	6034	5752	7623	5268	4806	4842	6702	585	1964	1116	1584	1107	1158	2128	678	1866	6734	6847	6678	7472	1740	685
1017.6	1517.2	1023.2	1288.6	1433.8	1206.8	1150.4	1524.6	1053.6	961.2	968.4	1340.4	261.6	392.8	223.2	316.8	221.4	231.6	425.6	303.2	373.2	1122.3	1141.2	1113.0	1245.3	290.0	279.7
1	1	1	1	1	1	1	1	FI.	1	1	1	0.5	1			1	F1	1	0.5	1	1	1	1		1	0.5
0	0	0	0	0	0	867	0	0	0	14907	0	93	371	18702	0	8673	0	0	5993	873	5984	10343	0	6180	770	335
0	0	0	0	0	0	241	0	0	0	4968	0	154	140	327	0	3595	0	0	2026	292	7060	2275	0	5726	432	148
20000	20000	20000	20000	20000	20000	0	20000	20000	20000	0	20000	0	0	0	20000	0	20000	20000	0	0	730	0	20000	1824	0	0
20000	20000	20000	20000	20000	20000	1108	20000	20000	20000	19875	20000	247	511	19029	20000	12268	20000	20000	8019	1165	13774	12618	20000	13730	1202	483
	4000.0	4000.0	4000.0	4000.0	4000.0	221.6	4000.0	4000.0	4000.0	3975.0	4000.0	152.4	228.5	3805.8	4000.0	2453.6	4000.0	4000.0	1603.8	233.0	2295.7	2103.0	3333.3	2288.3	200.3	197.2
1	1	1	1	1	1	1	1	1	1	1	1	0.3	0.5	1	1	1	1	1	1	1	1	1	1	1	1	0.5
9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	5	5	5	2	5	2
2	3	3	4	4	9	7	3	ŝ	4	4	9	7	7	m	ŝ	4	4	9	7	7	3	4	4	9	7	7
123832	123846	123837	123838	123839	123876	123877	123872	123833	123868	123849	123831	123840	123845	123945	123962	123984	123971	123985	123963	123975	123835	123844	123860	123857	123870	123854
		-	21C 70%RH 03+S02+N02+H2S+Cl2							21C 80%RH 03+S02+N02+H2S+Cl2						-	21C 80%RH Fluct. 03+502+N02	_					316 F00/BH F1+ 03. 503 MO3. H36. 613	210-20%MU LINCE 02+20012001		
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11. Index

$C _{y=0}$	Concentration of oxygen at the metal surface, mol/m ³
$c_{Cl} - _{y=0}$	Concentration of Cl^{-} at the copper surface, mol/m ³
$C_{O_2}^{sat}$	Saturation concentration of oxygen, mol/m ³
C ₀₂	Concentration of oxygen, mol/m ³
Ca	Concentration of a species in the aqueous phase, mol/m ³
C _{cl} -	Concentration of Cl^- , mol/m ³
c_i^{init}	Initial concentration of species i , mol/m ³
c_i^{sat}	Saturation concentration of species i , mol/m ³
C _i	Concentration of species i in the solution, mol/m ³
D _{Cl} -	Diffusion coefficient for Cl^- , m ² /s
D _{cucl} -	Diffusion coefficient for $CuCl^-$, m ² /s
D_{CuCl_2}	Diffusion coefficient for $CuCl_2^-$, m ² /s
D_{O_2}	Diffusion coefficient for oxygen, m ² /s
D _{OH} -	Diffusion coefficient for OH^- , m ² /s
D _e	Effective diffusion coefficient, m ² /s
D _i	Diffusion coefficient of species i , m ² /s
d _i	Non-dimensional diffusion coefficient of species <i>i</i> 241

$e^{0}_{O_{2} OH}$ -	Non-dimensional reduction potential of oxygen reduction
$E^{0}_{O_{2} OH}$ -	Standard reduction potential of oxygen reduction, V
E _{corr}	Corroding system potential, V
e _{corr}	Non-dimensional corrosion potential
$e^0_{Cu CuCl_2^-}$	Non-dimensional reduction potential of metal oxidation
$E_{Cu CuCl_2}^0$	Standard reduction potential of metal dissolution reaction, V
F	Faraday constant
<i>H^{cp}</i>	Henry's law constant
H _i	Henry's law coefficient
i	Current density, A/m ²
i ⁰ _{02 0H} -	Corresponding exchange current density, A/m ²
i _{02 0H} -	Current density for oxygen reduction, A/m ²
i ₀	Exchange current density, A/m ²
i _{corr}	Current density for corrosion rate, A/m ²
$i_{Cu CuCl_2^-}$	Current density for copper dissolution rate, A/m ²
j _{corr}	Non-dimensional corrosion current density
k	Rate constant

k_0	Coefficient
k _{diss}	Rate constant
k _G	Effective rate constant for crystal growth
L	Thickness of copper oxide, Angstrom
L ₀	Initial thickness of copper oxide, Angstrom
M _i	Concentration of a gas
n	Electrons transferred
n'	Order parameter dependent on crystal size and morphology
N _i	Flux of any species <i>i</i>
p	Partial pressure of that species in the gas phase under equilibrium, Pa
p_i	Partial pressure of the gas, Pa
P_j	Probability of finding a specific site
R	Gas constant
R _{diss}	Proton- or ligand-promoted dissolution rate
R_G	Rate of corrosion growth, mol/(cm ² \cdot s)
R _i	Production rate of species
S	Surface concentration of sites
t	Exposure time, s

Т	Temperature, K
t'	Actual test time, day
t_1	Thirty days
u _i	Mobility
v	Velocity of the liquid solvent, m/s
x	Measured film thickness after time t' , Angstrom
<i>x</i> ₁	Equivalent film thickness after 30 days, Angstrom
x _a	Mole fraction of dissolution active sites
у	Corrosion thickness
Ζ	Ionic charge
z _i	Charge of species
$\alpha_{O_2 OH}$ -	Transfer coefficient
γ _i	Activity coefficients
ε _e	Porosity
$ heta_i^{init}$	Non-dimensional initial concentration in the electrolyte layer
$ heta_i$	Non-dimensional concentration in the electrolyte layer
$ au_t$	Tortuosity of copper oxide
ψ_i	Non-dimensional flux of species <i>i</i>

Ø	Electronic potentials in the electrolyte, V
Δc	Degree of supersaturation of the product species
α	Transfer coefficients of the forward reaction
β	Transfer coefficients of the backward reaction
η	Overpotential, V
μ	Ionic strength
ξ	Non-dimensional vertical coordinate
ρ	Density of freely moving charge
τ	Non-dimensional time
AFM	Atomic Force Microscopy
ASHRAE	American Society of Heating, Refrigerating and Air-Conditioning Engineers
ASTM	American Society for Testing and Materials
BEESL	Building Energy and Environmental System Laboratory
EDS	Energy dispersive spectrometry
ESCA	Electron Spectroscopy for Chemical Analysis
FTIR	Fourier-transform infrared spectroscopy
HVAC	Heating, ventilation, and air conditioning
ISA	International Society of Automation

ITE	Information technology equipment
РСВ	Printed circuit board
QCM	Quartz crystal microbalance
RGB	Red, green, black color index
SEM	Scanning electron microscopy
SMT	Surface-mount technology
XPS	X-ray Photoelectron Spectroscopy

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EDUCATION

PhD, Mechanical Engineering, Syracuse University, USA | May 2021

MS, Mechanical Engineering, Syracuse University, USA | May 2016

B.S. Building Environment and Equipment Engineering (HVAC), Rank: 3/134, Shenyang Jianzhu University,

Chinal July 2014

PROJECTS

Integrated Whole-Building Energy Efficiency Retrofit Solution for Residences in Cold/Very Cold Climates September 2020 – Present

- Conduct the literature review on the standard measurement methods for air leakage and thermal performance of building envelope;
- Collaborate with the architects and construction company to design and develop the sample panel for energy efficiency retrofit solution;
- Setup the test facility of the mid-scale chamber and full-scale building testing. Build the data acquisition system to collect the data (temperature, heat flux, flow rate, and the pressure difference between the panel sides);
- Model the energy consumption for the retrofit building and indoor air quality;
- Incorporate with the multiple engineer teams to install the full-scale test assemblies, energy POD, and internal partitions.

Effects of Air Pollution on the Reliable Operation of Information Technology Equipment in
Data CentersJune 2016 – May 2019

- Researched how gaseous pollutants under different thermal conditions impact the reliability of information technology equipment in the data centers;
- Examined the literature of gas pollutants around the world and defined the "worst realistic pollutant concentration" (60ppb O₃, 80ppb NO₂, 40ppb SO₂, 2ppb Cl₂, and 10ppb H₂S). Explored corrosion mechanism for copper and silver;
- Cooperated with Purifil company and Clemson University to analyze corrosion performance;
- Developed a mixed flow gas test facility and designed the exposure chamber using a 3D printer;
- Performed measurements of Cu and Ag under various thermal environment and pollutant conditions;
- Detected the corrosion material geometry and chemical elements by SEM/EDS and AFM;
- Designed and built a coulometric reduction apparatus to measure the corrosion thickness on copper and silver coupon;

- Led the development of a photo box to take high-quality photos for coupons. Using MATLAB code, explored the relationship between the color's RGB values (red, green, and blue intensity) of coupons and corrosion thickness;
- Plan to create the mathematical simulation model for the corrosion process;
- Documented technical reports and summarized the testing results.

Data Analysis for the Airline Satisfaction

January 2019 – April 2019

- Used R to do the data preparation for a big data set and transform the data as needed;
- Made use of descriptive statistics to further study significant attributes;
- Using the modeling techniques (linear models, rules mining, etc. el) analyzed the correlation between satisfaction and attributes;
- Provided a written analysis with visualizations.

Definition of a Reference Residential Building Prototype for Evaluating IAQ and Energy
Efficiency StrategiesJanuary 2016 – June 2016

- Conducted the literature review on floor plans, building envelope, and construction methods (based on ASHRAE standards and 2014 Building America House Simulation Protocols);
- Used available modeling programs (Design Builder and Energy-plus) to define a reference residential building prototype for evaluating indoor air quality (IAQ) and energy strategies;
- Used Design builder and Energy-plus to simulate the building energy consumption.

Computational Fluid Dynamic (CFD) Validation of Heat Transfer around Manikin in MixedVentilationJune 2015 – December 2015

- Simulated the heat loss from manikin and predicted the performance of mixed ventilation using CFD modeling programs (Star CCM). Compared to the simulation results with benchmark data published in the literature;
- Improved the accuracy of the CFD results in terms of physical approximation errors, namely inlet boundary conditions, turbulence models, and spatial discretization errors;
- Studied independently a 2D bi-cubic interpolation algorithm to prescribe variable the boundary condition.

Intern – Guizhou Province Architectural Design & Research Institute

July 2013 - August 2013

- Implemented HVAC design software for the load calculation for a residential building;
- Acquired an understanding of the drawing standards for heat-supply engineering and heating, ventilation, and air conditioning.

SKILLS

Materials Characterization techniques: SEM/EDS, AFM. Modeling Tools: Energy plus, StarCCM (CFD), Design Builder. Software: SolidWorks, Microsoft Office, AutoCAD. Programming Languages: MATLAB, R, Python.

EXPERIENCE

- Syracuse University, doctoral researcher, June 2016 Expected May 2020.
- Syracuse University, teaching assistant (Introduction to MATLAB), February 2019 May 2019.
- Syracuse University, graduate researcher, June 2015 June 2016.
- Syracuse University, teaching assistant (Building Materials and Envelopes; Building Environmental Modeling), February 2016 May 2016.
- Shenyang Jianzhu University, HVAC designer for graduation project, April 2014 August 2014.
- Guizhou Province Architectural Design & Research Institute, HVAC designer intern, July 2013 August 2014.

PUBLICATIONS

- <u>Rui Zhang</u>, Jianshun Zhang, Roger Schmidt, Jeremy Gilbert and Beverly Guo, "Effects of Moisture Content, Temperature and Pollutant Mixture on Atmospheric Corrosion of Copper and Silver and their Implications for the Environmental Design of Data Centers", Science and Technology for the Built Environment, (2020) 0, 1-20.
- <u>Rui Zhang</u>, Roger Schmidt, Jeremy Gilbert and Jianshun Zhang, "Effects of Gaseous Pollution and Thermal Conditions on the Corrosion Rates of Copper and Silver in Data Center Environment: A Literature Review", 7th International Building Physics Conference, IBPC 2018.
- Ryan Milcarek, Shaun Turne, <u>Rui Zhang</u>, Jeongmin Ahn and Jianshun Zhang, "Publication Preview Source Predicting Envelope and Micro Cogeneration Performance in Future Climates", 2017 ASHRAE Annual Conference.
- Zhenlei Liu, <u>Rui Zhang</u>, Tim Stenson, Adib Rais, Wenhao Chen, Jianshun Zhang. 2017. Definition of a Reference Residential Building Prototype for Evaluating IAQ and Energy Efficiency Strategies. Healthy Building 2017. September 2-5. Tainan, Tawan.

ACTIVITIES

- Vice President, ASHRAE SU Student Branch, 2018
- Radio Announcer, Shenyang Jianzhu University, 2012 2014