The Role of Particles on Initial Atmospheric Corrosion of Copper and Zinc
-Lateral Distribution, Secondary Spreading and CO₂-/SO₂-influence

Zhuo Yuan Chen

Doctoral Thesis

Division of Corrosion Science
School of Industrial Engineering and Management
Royal Institute of Technology
SE-100 44 Stockholm, Sweden

Opponent: Ass. Prof. Jan-Erik Svensson, Dept. Chemical and Biological Engineering, Chalmers University of Technology, 412 96 Göteborg, Sweden

ISRN KTH/MSE – 05/77 – SE + CORR/AVH
ISBN 91-7178-155-2
The figure on the cover shows the optical micrograph of copper surface deposited with a NaCl particle after 6 hours of exposure to 80% RH pure air with <5 ppm CO₂.
Abstract

The role of sodium chloride (NaCl) particles and ammonium sulfate ((NH₄)₂SO₄) particles on the initial atmospheric corrosion of copper and zinc was investigated under in situ and ex situ conditions using microgravimetry, FTIR spectroscopy, ion chromatography, scanning electron microscopy with x-ray microanalysis and the scanning Kelvin probe. For the first time, in situ infrared spectra were collected on a micron level during particle induced atmospheric corrosion using a recently developed experimental set-up for in situ FTIR microspectroscopy. Lateral distribution of corrosion and reaction products on copper and zinc surfaces was determined and could be connected with the mechanisms of the initial particle induced corrosion. The recently discovered secondary spreading effect from NaCl electrolyte droplets on metal surfaces was studied under in situ conditions and the effect of CO₂ on the spreading process was elaborated. The ambient level of CO₂ (350 ppm, 1 ppm = 10⁻⁶ volume parts) results in a relatively low secondary spreading effect, whereas the lower level of CO₂ (<5 ppm) causes a much faster secondary spreading effect over a large area. At low CO₂ concentration alkaline conditions will prevail in the cathodic area, leading to large changes in the surface tension at the oxide/electrolyte interface in the peripheral parts of the droplet. This induces a surface tension driven convective flow of electrolyte from the NaCl droplet. The continuous growth of the secondary spreading area at low CO₂ concentration is possible due to the galvanic coupling with the droplet leading to transport of sodium ions to this region and maintenance of the alkaline conditions. At 350 ppm CO₂, carbonate formation in the secondary spreading area results in lowering of the pH, increasing the surface tension of the oxide/electrolyte interface and inhibiting the secondary spreading.

CO₂ strongly affects the NaCl-induced atmospheric corrosion rate of copper. The overall influence of CO₂ and NaCl depends on at least three identified mechanisms. At low NaCl particle density, CO₂ affects the secondary spreading effect from the electrolyte droplet. This leads to a larger effective cathodic area at low CO₂ concentration and a higher corrosion rate. The more alkaline surface electrolyte present at low CO₂ concentration also affects the formation of corrosion products and the amount of soluble copper chloride. Whereas the presence of larger amounts of soluble chloride tends to increase the corrosion rate, the formation of CuO results in a more protective surface film which decreases the corrosion rate. This effect was observed at higher NaCl particle densities, where the secondary spreading areas overlapped with adjacent NaCl particle clusters. The formation of CuO leads to lower corrosion rates compared to ambient CO₂ concentration in which this phase was not formed. For zinc, the formation of a more protective corrosion product layer was not observed and the corrosion rate is generally higher for low than for ambient CO₂ concentration.
The presence of NaCl particles on the metal surfaces strongly affects the SO$_2$ interaction with the metal surfaces. The oxidation of S(IV) turned out to be fast at the area of the NaCl-containing electrolyte droplet, both for copper and zinc. On copper surfaces, both sulphate (SO$_4^{2-}$) and dithionate (S$_2$O$_6^{2-}$) ions formed which is consistent with a copper catalysed reaction route for sulfite oxidation including the formation of a Cu(II)–sulfito complex as an important step. For zinc, a surface mediated sulfite oxidation process leads to rapid formation of sulphate in the electrolyte droplet area. The presence of SO$_2$ strongly inhibits the secondary spreading due to the decrease in pH induced by absorption of SO$_2$ in the cathodic areas. The presence of gaseous oxidants, such as NO$_2$ and O$_3$, has previously been considered as an important prerequisite for the oxidation of sulfite on copper. The results obtained here suggest that the formation of local electrochemical cells induced by deposited NaCl particles could be another important route for S(IV)-oxidation to sulfate formation. On copper, SO$_2$ was also found to promote the formation of less soluble copper chlorides, such as paratacamite (Cu$_2$(OH)$_3$Cl) and nantokite (CuCl). The electrolyte droplet was dried after 24 hours of exposure due to the formation of less soluble paratacamite (Cu$_2$(OH)$_3$Cl) and nantokite (CuCl) and led to a decrease in the corrosion rate. Thus, SO$_2$ alone promotes the corrosion rate of copper, whereas in the presence of NaCl particles the corrosion rate of copper may slow down due to the formation of insoluble copper chloride compounds. The lateral distribution of corrosion products after exposure of NaCl contaminated copper and zinc surfaces to humid air with gaseous pollutants is a result of the formation of local electrochemical cells at the particles and concomitant differences in chemical composition and pH.

For (NH$_4$)$_2$SO$_4$ deposited copper and zinc surfaces the corrosion effects increase with the amount of pre-deposited particles and with the exposure time. On copper, the size of the particles affects the corrosion rate, smaller particles resulting in a higher corrosion rate than larger particles at equal amount of deposition. The formation of Cu$_2$O was the dominant corrosion product after exposure longer than 10 days. (NH$_4$)$_2$SO$_4$ particles result in enhanced Cu$_2$O formation on copper due to a reaction sequence involving catalysis by NH$_3$. The corrosion of copper by (NH$_4$)$_2$SO$_4$ particles was much larger than that induced by NaCl particles. However, for zinc, the (NH$_4$)$_2$SO$_4$ particles lead to smaller corrosion effects than those of NaCl particles. For both particles, significant corrosion attack was observed at relative humidity (RH) lower than the deliquescence point of the salts.

KEY WORDS: atmospheric corrosion, copper, zinc, NaCl particles, (NH$_4$)$_2$SO$_4$ particles, humid air, SO$_2$, O$_3$, NO$_2$, CO$_2$, in situ FTIR microspectroscopy, FTIR spectroscopy, scanning Kelvin probe.
Preface

The following papers are presented in this thesis:

I. Z. Y. Chen, S. Zakipour, D. Persson and C. Leygraf, 
The Effect of Sodium Chloride Particles on the Atmospheric Corrosion of Pure Copper, 

II. Z. Y. Chen, S. Zakipour, D. Persson and C. Leygraf, 
The Combined Effects of Gaseous pollutants and Sodium Chloride Particles on the Atmospheric Corrosion of Pure Copper, 
Corrosion, accepted for publication.

III. Z. Y. Chen, D. Persson, A. Nazarov, S. Zakipour, D. Thierry and C. Leygraf, 
In Situ Studies of the Effect of CO2 on the Initial NaCl-induced Atmospheric Corrosion of Copper, 

IV. Z. Y. Chen, D. Persson, F. Samie, S. Zakipour and C. Leygraf, 
The Effect of Carbon Dioxide on Sodium Chloride Induced Atmospheric Corrosion of Copper, 

V. Z. Y. Chen, D. Persson and C. Leygraf, 
In situ Studies of the Effect of SO2 on the Initial NaCl-induced Atmospheric Corrosion of Copper, 

VI. Z. Y. Chen, J. Tidblad, D. Persson, S. Zakipour, V. Kucera and C. Leygraf, 
The Effect of Ammonium Sulfate Particles on the Atmospheric Corrosion of Copper, 
Manuscript.

VII. Z. Y. Chen, D. Persson and C. Leygraf, 
Initial NaCl Particle Induced Atmospheric Corrosion of Zinc-Effect of CO2 and SO2, 
Corrosion Science, submitted for publication.
The following papers have resulted from work that is not fully presented in the thesis:

VIII. Z. Y. Chen, D. Persson and C. Leygraf,  
The Effect of NaCl and (NH₄)₂SO₄ Particles on the Atmospheric Corrosion of Zinc,  
Manuscript.

IX. Z. Y. Chen, D. Persson, S. Zakipour and C. Leygraf,  
*In Situ* Studies of the NaCl-induced Atmospheric Corrosion of Copper Using FTIR Microspectroscopy,  
*16th International Corrosion Congress*, Beijing, China (2005)

X. C. Leygraf, S. Bertling, Z. Chen, M. Johnson and I. Odnevall Wallinder,  
Atmospheric Corrosion-New Fundamental and Environmental Aspects,  
*16th International Corrosion Congress*, Beijing, China (2005)
Contents

1. Introduction............................................................................................................. 1

2. Atmospheric corrosion of metals ...................................................................... 3
   2.1 General description of atmospheric corrosion ............................................. 3
   2.2 Influence of relative humidity ................................................................. 5
   2.3 Influence of gaseous pollutants (SO2, NO2 and O3) .................................. 6
   2.4 Influence of carbon dioxide ...................................................................... 8
   2.5 Influence of airborne particles ................................................................. 9

3. Experimental ...................................................................................................... 12
   3.1 Materials, sample preparation and particles deposition ......................... 12
   3.2 Laboratory exposures ............................................................................. 14
   3.3 Mass gain and mass loss measurements .................................................... 16
   3.4 Ion Chromatography ............................................................................. 17
   3.5 Scanning electron microscopy with X-ray microanalysis (SEM/EDAX) .... 17
   3.6 Fourier Transform Infrared Spectroscopy (FTIR spectroscopy) ............. 18
   3.7 Experimental set-up for in situ studies with FTIR microspectroscopy ...... 18
   3.8 In situ and ex situ scanning Kelvin probe .................................................. 21

4. Summary of papers ............................................................................................ 22
   4.1 Corrosion effects at relative humidities lower than the deliquescence point of the salt particles ................................................................. 22
   4.2 The secondary spreading effect from electrolyte droplet......................... 25
   4.3 NaCl particle induced atmospheric corrosion of copper in humid air-the role of CO2 ............................................................... 28
   4.4 The role of NaCl particles on the atmospheric corrosion of copper in humid air containing SO2 ................................................................. 30
   4.5 The role of NaCl particle on the atmospheric corrosion of zinc and the effect of CO2 and SO2 ............................................................... 32
   4.6 The role of (NH4)2SO4 particle on the atmospheric corrosion of copper in humid pure air ................................................................. 36
   4.7 Comparison of the corrosion effect of NaCl and (NH4)2SO4 particles on copper and zinc ................................................................. 37

5. Conclusions ........................................................................................................ 39

6. Acknowledgements ............................................................................................ 42

7. References .......................................................................................................... 44

Paper I-VII
1. Introduction

Copper and zinc are known to mankind from early ages and already in the Bronze Age (3000-1300 B.C.), people made tools and weapons using copper. Copper is one of the technologically most important metals. It is malleable, ductile, and a good conductor of heat and electricity (second only to silver in electrical conductivity). Copper and its alloys, brass and bronze have been extensively used in many applications, such as in microelectronic devices, circuit boards, and artistic, structural and architectural applications. The widespread use of copper has resulted in exposure of copper to corrosive conditions so it is important to understand atmospheric corrosion of copper in different environments. On exposure to natural environments copper surfaces develop a green surface layer of corrosion products, a patina, which are consequences of the complex interaction between the copper and the environment. The structure and composition of the patina has been a subject of numerous investigations. The formation of copper patina is a sequential process with initial formation of a thin layer of cuprite \((\text{Cu}_2\text{O})\). This layer causes the copper surface to lose its metallic color of copper and turn dull brown after a few days or months, depending on exposure conditions. After several years, other phases are formed in the corrosion product layer. It is known that in rural and less polluted urban atmospheres, the patina mainly consists of cuprite and copper hydroxy sulfates, such as brochantite \((\text{Cu}_4(\text{OH})_6\text{SO}_4)\) and anthlerite \((\text{Cu}_3(\text{OH})_4\text{SO}_4)\). In marine environments copper hydroxyl chloride is an important component in addition to cuprite and copper hydroxy sulfates.

Zinc is a bluish-white, lustrous metal. It is brittle at ambient temperatures but is malleable at 100 to 150°C. Zinc is an important material and it has been extensively used in many applications. Zinc is widely used as an alloying element, such as brass and the first use of zinc or this application can be dated to 500 B.C. The alloy brass contains copper and anywhere from 20-45% of zinc, depending on the type of brass. Brass is easy to work and is a good electrical conductor. Zinc alloys with many other metals. Nickel silver, commercial bronze, spring brass, and soft solder all contain zinc. Zinc metal is used for dry batteries, roof cladding, and to protect iron structures from corrosion by attaching zinc as sacrificial anodes. A large proportion of all zinc, perhaps more than a third, is used to galvanize metals such as iron to prevent corrosion. Zinc protects any exposed iron sacrificially because of the relative positions of zinc and iron in the electrochemical series. Due to its wide practical applications, much work has been performed on the corrosion of zinc materials during field exposures as well as in controlled laboratory environments. The corrosion products formed on zinc are a subject of numerous investigations. A freshly prepared zinc surface is covered by zinc oxide.
(ZnO) which is a relatively protective corrosion product with a thickness of a few nanometers (1 nm = 10^{-9} m). Within a few hours of exposure to humidified atmosphere, a thin layer of a zinc hydroxycarbonate (hydrozincite, Zn_5(OH)_6(CO_3)_2) will be formed on the zinc surface. The prolonged exposure of zinc can proceed along a variety of different paths of reaction sequences and the formation of corrosion products depend on the actual deposition rates of atmospheric constituents. Among these Cl^- and SO_2 are the most important stimulators. In a relatively benign rural atmosphere, the hydrozincite may continue to grow slowly followed by the formation of basic zinc sulfate, eg., Zn_4(OH)_6SO_4·H_2O. In a marine atmosphere, basic zinc chloride, Zn_5(OH)_6Cl_2·H_2O can be formed within days of exposure. Within weeks of exposure, basic zinc chlorosulfate, NaZn_4Cl(OH)_6SO_4·6H_2O, may be observed^{31,32}.

In this doctoral thesis, the role of particles (sodium chloride, NaCl and ammonium sulfate, (NH_4)_2SO_4) on the initial atmospheric corrosion of copper and zinc was investigated under in situ and ex situ conditions using microgravimetry, FTIR spectroscopy, ion chromatography, scanning electron microscopy with x-ray microanalysis and scanning Kelvin probe. For the first time, FTIR microspectroscopy was used for in situ studies of the NaCl induced atmospheric corrosion of copper and zinc and the effect of CO_2 and SO_2 on the initial corrosion process was investigated. The secondary spreading of the NaCl electrolyte from the peripheral part of the droplet was studied and a strong influence of the CO_2 concentration on the secondary spreading behavior was demonstrated. The effect of CO_2 on NaCl-induced atmospheric corrosion was elaborated in detail and the difference in corrosivity of (NH_4)_2SO_4 and NaCl particles was studied.
2. Atmospheric corrosion of metals

2.1 General description of atmospheric corrosion

Atmospheric corrosion is an important degradation process, which causes damage to equipment and structures. Structural elements in electronic devices, control systems and communications hardware are often very small, with dimensions or separations in the micrometer or sub-micrometer range. As a result, very small amounts of atmospheric corrosion products, amounts that can be detected only by highly sensitive analytical technique, may cause detrimental effects, and often result in electronic or thermal contact failures or electromagnetic shielding problems.\(^{46-47}\) It has been reported that more than half of the national cost of corrosion, which has been estimated at close to 4% of a nation’s gross domestic product, is a result of atmospheric corrosion.\(^{48}\) As another example, around 20% of failures of aircraft electronics are thought to be due to corrosion-related causes.\(^{49}\) It is difficult to estimate the cost of direct or indirect consequences caused by atmospheric corrosion on materials exposed in our environments.\(^{46}\) It has become evident that acid deposition through rain, snow, fog, or dew has resulted in substantial deterioration of artistic and historic objects, including old buildings and structures of historic value, statues, monuments and other cultural resources.

The atmospheric corrosion of metals is an electrochemical process in which a metal reacts with its environment to form an oxide or other compounds. To cause this process, there are four essential constituents: an anode, a cathode, the metal itself and an electrically conducting solution. Simply, the anode is the site at which the metal is corroded; the electrolyte solution is the corrosive medium; and the cathode forms the other electrode of the cell and is not consumed in the corrosion process. At the anode the corroding metal passes into solution as positively charged ions, releasing electrons that participate in the cathodic process. The distribution of anodic and cathodic areas is one of the most important factors determining the type of corrosion that occurs. But in the simplest case, general corrosion, the corrosion cells are very small and numerous, and distributed in a random manner over the surface of the metal, and the effect is more or less a uniform attack on the surface.

For the most corrosion processes, the anodic and cathodic reactions are the following:

\[
\begin{align*}
M \rightarrow M^{n+} + ne^- & \quad \text{Anodic reaction} \\
O_2 + 2H_2O + 4e^- \rightarrow 4OH^- & \quad \text{Cathodic reaction}
\end{align*}
\]
However, at low pH environment, hydrogen evolution may take place as cathodic reactions on the metal surface

\[ 2H^+ + 2e^- \rightarrow H_2(g) \]

Metals exposed in the environment will absorb water forming a thin water layer on the surfaces. The amount of water adsorbed by the metal surface is very important for the atmospheric corrosion process and most metals rapidly adsorb the first monolayer of water by forming a surface hydroxyl layer. Subsequent water adsorption is similar for many metals and oxides, and the water is adsorbed in the molecular form. At 20% RH there will be about one monolayer of water and at 75% RH there will be about five monolayers adsorbed on the metal surface. Adsorbed water films, which are thicker than three monolayers have properties similar to bulk water. Airborne salt particles, deposited on the surface of metals, will dissolve into this water adlayer and form thicker electrolyte layers or droplets. Oxygen (O\(_2\)), carbon dioxide (CO\(_2\)), and gaseous pollutants, such as SO\(_2\), O\(_3\) and NO\(_2\), dissolve into the adlayer and affect the corrosion process. Unevenly distributed water films lead to the formation of local electrochemical corrosion cells with spatially separated anodes and cathodes. This will occur in connection with the deposition of particles on the surface. This is illustrated in figure 1.

![Figure 1](image-url)  
**Figure 1.** Schematic picture of salt particle induced atmospheric corrosion.
2.2. Influence of relative humidity

The relative humidity (RH) in the atmosphere plays an important role and affects directly the amount of water on the metal surface\textsuperscript{11, 50}. It was reported\textsuperscript{11} that the atmospheric corrosion rate of metals increases with the relative humidity during the environmental atmosphere exposure. The presence of water is necessary for the atmospheric corrosion process and the water layer acts as a medium for electrochemical reactions as well as a solvent for atmospheric constituents. By definition, when relative humidity is 100\%, the air is saturated with water. If the water content in the air is increased the air will be super-saturated and water condensation will occur on any surface present, assuming that the surfaces are at the same temperature as the air. The formation of adsorbed layers of water on oxide covered and hydroxylated metal surfaces has been studied in several investigations\textsuperscript{50-53}. Lee and Staehle\textsuperscript{51} measured the water adsorption on an iron surface at different temperatures and concluded that the amount of water on the surface was only weakly dependent on the temperature. On the other hand, Strekalov\textsuperscript{52} showed that the amount of water on zinc decrease 3 times between 5 to 80 °C.

The presence of hygroscopic salt particles leads to absorption of water and formation of bulk electrolyte layer on the surface. This is usually accompanied with an abrupt increase in the corrosion rate of the metal. When a substance is dissolved in a solvent, such as water, a decrease in the vapour pressure of the solvent is observed:

\[
P_{\text{solvent}} = a_{\text{solvent}} P_{\text{solvent}}^0
\]

The vapour pressure of the solvent (\(P_{\text{solvent}}\)) is equal to the vapour pressure of the pure solvent (\(P_{\text{solvent}}^0\)) multiplied by the activity of the solvent in the solution (\(a_{\text{solvent}}\)). The vapour pressure lowering has very important consequences for the formation of surface electrolyte layers on metal surfaces. The water in a solution in contact with air with a certain relative humidity will try to reach the activity corresponding to that of the surrounding air. The concentration of a solution and the thickness of the surface film will therefore change with the relative humidity for given amount of salt on a surface. Salts such as NaCl will form solutions above a certain critical relative humidity called the deliquescence point. The deliquescence point at a given temperature is defined as the water activity of a single electrolyte solution that is in equilibrium with its salt precipitate. It was shown by Wexler and Seinfeld\textsuperscript{54} that the deliquescence point of a salt in a multicomponent solution is always lower than its deliquescence point in the solution alone. This is very
important under field conditions when mixture of pollutants can be present. Humidity sorption measurements with quartz crystal microbalance on gold surface exposed outdoors showed the presence of considerable amounts water at 40-50% RH due to water uptake of deliquescent particles on the surface.

The formation of non-uniform surface electrolyte such as droplets may occur during deposition of aerosols and hygroscopic particles on metals surface. Neufeld et al. studied the initiation mechanism of atmospheric corrosion of zinc after deposition of sodium chloride particles. The droplet creates a situation with a differential aeration cell with the anode in the center of the droplet and the cathodic areas in the peripherical parts of the droplet. A secondary spreading of electrolyte outside the initially formed droplet was observed. The secondary spreading included transport of cations to the spreading area outside the droplet but not of anions. In the present work, the secondary spreading of the NaCl electrolyte from the peripheral part of the droplet was studied in situ on copper and zinc surface and it was strongly affected by CO₂ concentration in the absence of SO₂. Ambient level of CO₂ (350 ppm) resulted in a relatively low secondary spreading effect, whereas the lower level of CO₂ (<5 ppm) caused a much faster secondary spreading effect over a large area. In the presence of SO₂, a small secondary spreading effect of NaCl electrolyte on copper surface from the edge of the droplet was observed, whereas there is no secondary spreading effect on zinc surface. No secondary spreading effect of (NH₄)₂SO₄ electrolyte was observed. CO₂ did not affect the secondary spreading behaviour of the NaCl electrolyte droplet in the presence of SO₂. The droplet formation is related to the wettability of the surface. A drop of water would spread on a surface with high surface energy. Cole et al. monitored the changes in surface energy during short-time exposures to humid air and concluded that there was a correlation between the corrosion rate and surface energy of the galvanised steel surface.

2.3. Influence of gaseous pollutants (SO₂, NO₂ and O₃)

Many atmospheric gaseous pollutants that occur in our everyday environment can act as corrosion stimulators. Several gaseous pollutants known to accelerate corrosion attacks are produced by human activities and are, thus, present in larger amounts in urban and industrial areas. Sulphur dioxide (SO₂), nitrogen dioxide (NO₂) and ozone (O₃) are most important gaseous pollutants for the atmospheric corrosion of metals. SO₂, O₃ and NO₂ present in the air can dissolve into the water layer formed on the metal surface, resulting in destabilisation of surface oxides and initiation of corrosion.
Low concentrations of gaseous pollutants influence the reliability of electronic equipment exposed in the atmosphere. This fact is, to some extent, clear from international standards\textsuperscript{59}, where limits for chemically active pollutants given are of the same order of magnitude as those given by WHO concerning human health. Due to synergistic effects, sensitivity of some equipment exposed in the atmosphere is, however, often higher than is understood from limits given in standards.

SO\textsubscript{2} is a colourless gas with a sharp, irritating odour. It is produced from the burning of fossil fuels (coal and oil) and the smelting of mineral ores that contain sulfur. Erupting volcanoes can be a significant natural source of SO\textsubscript{2} emissions. SO\textsubscript{2} is an acidic gas and it is a major component of acid rain since it mixes with water vapour in the atmosphere, reacting to produce sulphuric acid (H\textsubscript{2}SO\textsubscript{4}). This is possible as UV radiation in the upper atmosphere catalyses the reaction between SO\textsubscript{2} and O\textsubscript{2} to produce sulphur trioxide which then reacts with water. Great efforts have been done to reduce SO\textsubscript{2} emissions with desulphurisation of fuels to help reduce the acid rain effect.

The interest in the effect of SO\textsubscript{2} on atmospheric corrosion stems to a large extent from its role as one source for sulfate which is usually found in the corrosion products of metals exposed, indoors and outdoors, to the urban atmosphere. Despite the decrease in the SO\textsubscript{2} levels in many countries, sulphates are still a major corrosion product found on surfaces of copper, zinc and other metals exposed in the atmosphere, indicating that SO\textsubscript{2} still plays a very important role for the atmospheric corrosion. It was early understood that the corrosion rate of copper, zinc and other metals in the atmosphere is related to the concentration of SO\textsubscript{2}. The mechanism by which SO\textsubscript{2} accelerates the corrosion of copper, zinc and other metals is still not fully understood, although a great number of investigations have been devoted to this subject\textsuperscript{8-15, 60-67}. The corrosion stimulating effect of SO\textsubscript{2} is usually attributed to the acidification effect of the solvated SO\textsubscript{2} and its oxidised forms and it was suggested already in the early work by Vernon\textsuperscript{60-61} that the oxidation of SO\textsubscript{2} to produce SO\textsubscript{4}\textsuperscript{2-} influences the local pH on the surface. This causes oxide dissolution and increases the corrosion rate. However, in controlled laboratory exposures, the reactions of SO\textsubscript{2} of copper in the absence of additional oxidants produce copper sulfites as the main reaction product\textsuperscript{62-65} and the oxidation of these copper sulfite layers to sulfate is quite slow in clean humid air.

Nitrogen dioxide, NO\textsubscript{2}, and ozone, O\textsubscript{3}, are also very important gaseous pollutants because they are among the most important trace oxidants in the atmosphere and are able to accelerate atmospheric corrosion in the presence of SO\textsubscript{2}. NO\textsubscript{2} is a brown, acidic and highly-corrosive gas that can affect our health and environment. Nitrogen oxides are critical components of photochemical smog — NO\textsubscript{2} produces
the yellowish-brown colour of the smog. NO\textsubscript{2} can be oxidised and form nitric acid (HNO\textsubscript{3}), which is very corrosive to materials. Ozone is a colourless, highly reactive gas with a distinctive odour. It is formed naturally by electrical discharge (lightning) and in the upper atmosphere at altitudes of between 15 to 35 km. The stratospheric O\textsubscript{3} protects the Earth from harmful ultraviolet radiation from the sun. However at ground level, elevated levels of O\textsubscript{3} are produced by photochemical reactions involving other air pollutants. Given sunlight and suitable meteorological conditions, nitrogen oxides and volatile organic compounds can react to form photochemical oxidants (also known as photochemical smog) of which O\textsubscript{3} is the principal component.

NO\textsubscript{2} and O\textsubscript{3} are believed to play important roles as oxidants of SO\textsubscript{2}. As showed in several investigations, they can have synergistic effects with SO\textsubscript{2} and increase the corrosion rate several times\textsuperscript{9-12}. Another route for SO\textsubscript{2} oxidation could be a metal-catalyzed reaction, which is an important pathway in atmospheric microdroplets\textsuperscript{68}.

\textbf{2.4. Influence of carbon dioxide}

The concentration of carbon dioxide (CO\textsubscript{2}) in the ambient atmosphere is about 350 ppm. Most of the CO\textsubscript{2} results from the combustion of organic matter if sufficient amounts of oxygen are present. Dissolved CO\textsubscript{2} in the water forms weak carbonic acid (H\textsubscript{2}CO\textsubscript{3}) and the carbonic acid in turn dissociates partly to form bicarbonate (HCO\textsubscript{3}\textsuperscript{-}) and carbonate ions (CO\textsubscript{3}\textsuperscript{2-}).

CO\textsubscript{2} is one of the most important parameters in determining corrosivity of an oil/gas production environment. CO\textsubscript{2} is commonly injected into or adjacent to producing oil wells. It will act as both a pressurizing agent and when dissolved into the underground crude oil will significantly reduce its viscosity, enabling the oil to flow more rapidly through the earth to the removal well. In mature oil fields extensive pipe networks are used to carry the CO\textsubscript{2} to the injection points. The most important role of CO\textsubscript{2} on atmospheric corrosion is to participate in the formation of secondary products, especially on non-ferrous metals. Kaesche\textsuperscript{69} discussed this point and concluded that the dissolution of CO\textsubscript{2} gave an electrolyte pH of between 5 and 5.6. If oxygen is present in excess, the cathodic reaction will not change at this pH from oxygen reduction to hydrogen reduction. Recently, it was reported that CO\textsubscript{2} has a strong effect on the NaCl-induced atmospheric corrosion of metals\textsuperscript{34, 70-73} and the corrosion was considerably lower at low CO\textsubscript{2} concentrations than at ambient. In reality, the supply of CO\textsubscript{2} can be restricted under certain conditions such as in crevices and confined surfaces and under paint films which could lead to high corrosion rates in these locations. The studies of the effect of CO\textsubscript{2} on the NaCl-induced atmospheric corrosion of metals may help in
understanding crevice corrosion, pitting corrosion and corrosion beneath organic coatings and deposits where the supply of CO₂ could be limited. Moreover, the studies can also provide important information when accelerated tests for the atmospheric corrosion of metals are developed. It was reported that the ambient concentration of CO₂, 350 ppm, inhibit the NaCl-induced corrosion of metals. Falk et al. showed that in the absence of NaCl, 350 ppm CO₂ enhanced the corrosion rate of zinc slightly. This slight corrosive effect of CO₂ is caused by the acidification of the surface electrolyte, giving rise to higher surface conductivity and an enhanced dissolution of surface films. On the contrary, in the presence of NaCl particles, CO₂ made the corrosion rate of zinc slow down. Lindström et al. reported that the corrosion rate of zinc at 22°C was 3-4 times smaller in air containing 350 ppm CO₂ compared with CO₂-free air in the presence of 70 µg/cm² NaCl particles. In the case of aluminum, CO₂ was also found to inhibit the NaCl-induced atmospheric corrosion. In the presence of 14 and 70 µg/cm² NaCl particles, the corrosion rate in CO₂-free humid air was 20 times higher compared to air containing ambient levels of CO₂. Similar results were also reported for magnesium alloys. Ambient levels of CO₂ strongly influenced the NaCl-induced atmospheric corrosion of magnesium alloys due to the formation of slightly soluble carbonate-containing corrosion products that provide a partly protective layer on the surface. As part of this doctoral thesis, the effect of CO₂ on the NaCl particles induced atmospheric corrosion of copper was studied and it was found that the effect is complex. With lower amount of NaCl particles on the copper surface (<15 µg/cm²), the corrosion rate was higher with <1 ppm CO₂ than with 350 ppm CO₂, and for higher amount of NaCl (>15 µg/cm²), the corrosion was higher with 350 ppm CO₂. In contrast to NaCl, no effect of CO₂ on the (NH₄)₂SO₄-induced atmospheric corrosion of zinc and copper was observed.

2.5. Influence of airborne particles

Particles exist everywhere in our environment and many airborne particles can act as corrosion stimulators. There are several processes which may lead to increase of atmospheric corrosion rate by particles: (1) a direct or indirect effect on the metal; (2) influence on capillary condensation; (3) the formation of nuclei of condensation. Concerning the first process, three types of particles can be distinguished: (a) corrosion-active particles (mineral salts such as NaCl and (NH₄)₂SO₄); (b) corrosion-non-active particles but capable to adsorb active gases from the atmosphere (for example, coal/charcoal); and (c) neutral particles with low adsorption ability (such as Si). The deposition of particles (a) and (b) on the metal surfaces will lead to acceleration of corrosion rate (in the case of group (b)
because of acceleration of SO$_2$ adsorption). Particles from group (c) are not very dangerous to corrosion for many metals. However for metals in which passivity is determined by free access of oxygen to the surface (e.g. stainless steel), the deposition of such particles can sharply increase the rate of corrosion. Such particles on the surface lead to the formation of thin crevices and cracks in which the rate of the anodic reaction increases significantly compared to the surface with easy access to oxygen. Localised attack can be promoted on the metal due to the effect of differential aeration cells. Concerning soluble salts, such as NaCl particles, the hygroscopic properties of the salts strongly influence the formation of surface electrolyte.

Airborne salt particles have been reported to play an important role for atmospheric corrosion. Concentrations of gaseous pollutants, such as SO$_2$, NO$_2$ and O$_3$, are being reduced in many regions, and the relative importance of salinity particles is thus increasing. Sodium chloride (NaCl) and ammonium sulphate ((NH$_4$)$_2$SO$_4$) particles are probably the most important airborne salt particles for atmospheric corrosion. Chloride deposition is a major contributor to the increased atmospheric corrosivity in marine environments. The main source for chlorine in the atmosphere is sea aerosol salt$^{36}$. Chlorides enter into the atmosphere in tiny droplets of salt solution originating from surf action and turbulent ocean states, and are transported inland predominantly by coastal wind patterns as solid particles or liquid droplets. Sodium chloride and calcium chloride (CaCl$_2$) are also used to remove snow and ice on roads. As a result, large amounts of chloride may be deposited on the objects close to the roads. Chlorides do not reduce the pH of the electrolyte on the metal surfaces, but provide a rather corrosive electrolyte with a high conductivity. (NH$_4$)$_2$SO$_4$ particles are also very important for atmospheric corrosion because ammonium and sulphate are the most abundant ions found in aerosol particles. NaCl and (NH$_4$)$_2$SO$_4$ particles can be used as corrosion stimulators in accelerated tests of metals. The former can be used as the accelerated testing for environments which are close to the seaside and have high amount of chloride. (NH$_4$)$_2$SO$_4$ particles can be used in accelerated tests for environments which are far away from the seaside and have no or only small amount of chloride. Due to their importance, much work has been done to explore the effect of sodium chloride and ammonium sulphate particles on the atmospheric corrosion of metals$^{19-25, 34-40, 70-77}$. Lobnig et al.$^{21-23}$ showed that the corrosion products developed on copper covered by (NH$_4$)$_2$SO$_4$ particles are cuprite and basic copper sulphates and the fraction of cuprite in corrosion products increased with the exposure temperature. Tidblad and Graedel$^{25}$ in computer model calculations reported that the expected dominant corrosion products of (NH$_4$)$_2$SO$_4$ particles induced atmospheric corrosion of copper are antlerite and cuprite. The amount of antlerite formed depends only on the
amount of ammonium sulphate. All sulphate reacts to form corrosion products. On the other hand, the amount of cuprite formed is extremely sensitive to experimental conditions and uncertainties in the kinetic parameters. However, no study provided the quantitative results of the (NH$_4$)$_2$SO$_4$ induced atmospheric corrosion. An important reason is that the (NH$_4$)$_2$SO$_4$ particles cannot easily be distributed evenly onto the surface of the sample, which leads to low reproducibility in the determination of the corrosion rate.

Lindström et al.\textsuperscript{38} showed that the corrosion rate of zinc was strongly dependent on the nature of the cation with the higher corrosion rate obtained for sodium chloride and sodium sulphate in comparison to other salts of these anions. Eriksson et al.\textsuperscript{19} showed that the addition of small amounts of sodium chloride caused a marked increase in the corrosion rate of bronze in humid air. Strandberg and Johansson\textsuperscript{20} have studied the effect of NaCl in combination with O$_3$ and SO$_2$ and found that the corrosion effect was proportional to the amount of NaCl. In the presence of small amounts of NaCl, the corrosion rate slowed down when SO$_2$ was added. The corrosion rate was high with O$_3$ + SO$_2$ without NaCl, but decreased with small amounts of NaCl particles present on the surface. The results indicate that corrosion in a multi-pollutant situation in combination with NaCl particle deposition is complicated and that the rate controlling factors are different with and without electrolyte forming particles present on the surface.
3. Experimental

3.1 Materials, sample preparation and particles deposition

The copper and zinc samples used for laboratory exposures were of 99.9% purity and of 50×10×0.5 mm in size and the samples used for in situ FTIR microspectroscopy measurements were of 38×19×0.5 mm. Prior to exposure each sample was mechanically abraded and/or diamond polished. All samples were then ultrasonically cleaned in acetone of analytical grade for about 3 minutes, dipped in isopropanol of analytical grade for about 5 minutes, and then dried with a hair drier. The samples were stored in a desiccator with silica gel for about 24 hours before exposure.

For the laboratory exposures, NaCl particles were deposited by the following procedure. Small quantities (20 µl) of a saturated solution of NaCl in 99.5% ethanol were distributed onto the copper surface using a transfer pipette. The ethanol volatilized, whereby NaCl particles deposited on the copper surface. The volume of NaCl solution determined the total amount of NaCl deposited, which was determined gravimetrically. Deposition of NaCl under the conditions described, resulted in evenly distributed circular particle clusters with diameters of approximately 100 µm. The clusters consisted of individual NaCl particles of size less than 10 µm. Figure 2 displays scanning electron microscopy picture of copper after deposition of 4 µg/cm² of NaCl.

For in situ FTIR microspectroscopy measurements, a NaCl particle crystal, with a dimension in the range of (300-400)×(300-400)×(300-400) µm, was directly placed on the surface of the sample before in situ measurements.

The deposition of (NH₄)₂SO₄ particles is very important in the present study. In order to obtain a good reproducibility in the corrosion experiments the particles have to be distributed evenly on the copper surface. In the present study, a very simple and effective way was found to deposit (NH₄)₂SO₄ particles as follows. 200 mg (NH₄)₂SO₄ particles were carefully ground by hand into small powder and suspended in a 10 ml 99.7% ethanol solution. Two methods were used to obtain different size of particles. The first way was to expose the particle/ethanol suspension for 15 minutes in an ultrasonic bath. After that, the bottle holding the suspension, was put on a table for 1 hour. During this time, the larger particles deposited onto the bottom of the bottle while the smaller particles were kept suspended in the ethanol. After 1 hour a small amount of the suspension was deposited onto the surface of copper using a transfer pipette. The second way was to shake the solution by hand and then wait for 10 minutes. The suspension was
Figure 2. Scanning electron micrograph of copper deposited with 4 µg/cm² NaCl particles.

Figure 3. Scanning electron micrograph of copper deposited with small (NH₄)₂SO₄ particles (200 mg (NH₄)₂SO₄ particles powder mixed in 10 ml 99.7% ethanol, and then ultrasonically vibrated for 15 minutes.).
then deposited onto the copper surface. Moving the copper sample made the solution evenly distributed onto the copper surface. The ethanol volatilized, whereby (NH$_4$)$_2$SO$_4$ particles deposited on the copper surface. The amount of (NH$_4$)$_2$SO$_4$ particles deposited was measured gravimetrically. The reproducibility of the deposition is very good. Deposition of ultrasonically vibrated (NH$_4$)$_2$SO$_4$ particles under the conditions described here resulted in evenly distributed particles with size of approximately < 10 µm. On the other hand, deposition of (NH$_4$)$_2$SO$_4$ particles shaken by hand resulted in less evenly distributed particles with size of approximately < 100 µm. Figure 3 and 4 show the small and large particles after deposition.

### 3.2 Laboratory exposures

A schematic diagram and a photo of the apparatus used for laboratory exposures are shown in figure 5. It consists of three glass chambers of 5 litres each, in which three simultaneous exposures in humidified air can be performed. A constant temperature was maintained by means of a thermostatically controlled water bath.
Figure 5. Schematic diagram and photograph of the experimental set-up for the corrosion exposures.
that surrounded each test chamber. After passing an oil filter, two particulate filters (3 and 0.01 µm, respectively), and a charcoal filter, the decontaminated laboratory pure air was divided into three major streams, each passing through a humidifier. The relative humidity (RH) was changed by adjusting the temperature of a small water bath, which cools down the water vapour. The relative humidity was measured by a temperature/humidity sensor. SO$_2$ and NO$_2$ were generated by permeation tubes, while O$_3$ was generated by using a Hg lamp as ultraviolet (UV) source (Permakemi 5501). The humidified pure air and SO$_2$-, NO$_2$- and O$_3$-containing streams passed through mixing kettles and pre-cooling glass coils located in the thermostatically controlled bath, before the air passed upwards over the samples. These were evenly spaced and hung vertically, parallel to the air-flow. The concentration of pollutants was analyzed at the chamber outlet with an SO$_2$ (Thermo Environmental 43C), NO$_2$ (Thermo Environmental 42C), or O$_3$ (Thermo Environmental 49C) analyzer. The SO$_2$/NO$_2$ analyzers were calibrated using the permeation rate and the gas flow rate, determined by weighing the permeation tube intermittently and by an air-flow rate meter, respectively. The O$_3$ analyzer was calibrated using a standard UV source from ITM, an air pollution laboratory at Stockholm University, Sweden. The CO$_2$ concentration was monitored using a CO$_2$-analyzer (Testo 535). To reduce the CO$_2$ concentration in the air, it was passed through three bottles containing 2M NaOH solution, before the exposure air passed through the humidifier. The NaOH solution reacted with the CO$_2$ in the air, reducing the concentration of CO$_2$ to <1 ppm during the exposure. In order to obtain ambient CO$_2$ concentration, 350 ppm, a small flow of 2.5% CO$_2$ from a CO$_2$ gas cylinder was added into the exposure air. The laminar flow of air passed along the samples with a velocity of about 3 cm/min. All samples were exposed at a temperature of 25°C. At each exposure condition 3 parallel samples were used.

3.3 Mass gain and mass loss measurements

The corrosion effect on copper and zinc samples after laboratory exposure was determined quantitatively by measuring their increase and decrease in weight. Mass gain is the difference of the mass before (after deposition of particles) and after exposure. Mass loss is the difference between the original mass (before deposition of particles) and the mass after all corrosion products are removed, i.e., the total mass of the metal consumed during the corrosion process. Each sample was weighed before and after the deposition of particles, after the laboratory exposure and after removing the corrosion products. A microbalance with a ±2 µg-specified precision (±0.2 µg/cm$^2$ in this study) was used for the weight measurements. The weighing was performed in a heated room with a nearly constant temperature of
25±2°C and low relative humidity (<40%). The following weighing procedure was used. First, a reference sample of stainless steel was weighed (weight \(A_1\)). Then, the test sample was repeatedly weighed two times (weight \(B_1\) and \(B_2\)). Finally, the reference sample was weighed again (weight \(A_2\)). After deposition, exposure or removing all corrosion products, the weight of the test sample had changed. The test sample was weighed again (weight \(B_3\) and \(B_4\)) with the same procedure and the same reference (weight \(A_3\) and \(A_4\)). The mass gain or loss of the test sample was then calculated by the following equation:

\[
\frac{(B_3 + B_4) - (B_1 + B_2)}{2} - \frac{(A_3 + A_4) - (A_1 + A_2)}{2}
\]

Corrosion products formed on the copper surface after exposure were removed by pickling the samples in 5% sulfaminacid (\(\text{H}_2\text{NSO}_3\text{H}\)) solution in an ultrasonic bath followed by water and ethanol rinses. Corrosion products formed on zinc surface after exposure were removed by pickling the samples in 20% glycine (\(\text{H}_2\text{NCH}_2\text{COOH}\)) solution (250 g glycine + 1 L water) in an ultrasonic bath followed by water and ethanol rinses. The limited removal of bulk metal during the pickling procedure was corrected by pickling non-exposed samples as well.

### 3.4 Ion Chromatography

Water-soluble chloride or sulfate in the corrosion products after exposure was leached in ultra pure water using ultrasonic agitation. Analysis of chlorides and sulfate was performed using an Ion Chromatography model MetroOhm with a 733 IC Separation Center, 709 IC pump and 752 Pump Unit. The Column was a 6.1006.5\text{X}0 \text{Metrosep A Supp 5} and the eluent was a 3.2 mM \(\text{Na}_2\text{CO}_3/1.0\) mM \(\text{NaHCO}_3\) solution with 5% acetone. Detection was done with an electric conductivity detector model Metrohm 732 IC Detector.

### 3.5 Scanning electron microscopy with X-ray microanalysis (SEM/EDAX)

Samples were analyzed using a JEOL JSM-820 scanning electron microscope equipped with a Vantage Digital Microanalysis and a Pioneer Norvar detector. The working distance was 39 mm, the take-off angle 40° and the accelerating voltage 15 kV.
3.6 Fourier Transform Infrared Spectroscopy (FTIR spectroscopy)

The analysis of corrosion products on metal surfaces was made both with infrared reflection measurements and with FTIR microspectroscopy, the latter providing a more local information of the chemical composition (area smaller than 250×250 μm). The FTIR measurements were performed using a Biorad FTS175C spectrometer equipped with a UMA 500 microscope. The microscope was mounted onto the side of the Bio-Rad 175C spectrometer bench, and was equipped with a broad band mercury cadmium telluride (MCT) detector. The infrared reflection absorption spectroscopy (IRAS) measurements were made using a Seagull multireflection accessory with a KRS-5 wire grid polariser. P-polarised light with an angle of incidence of 78º was used for the analysis of the thin surface films. The microspectroscopy measurements were performed using a 15X cassegrain objective which provided an angle of incidence on the sample surface in the range from 15º to 35º. Spectra were obtained in the reflectance mode by adding 256 interferograms at 8 cm\(^{-1}\) resolution. The spectra are presented in absorbance units which correspond to \(-\log(R/R_0)\), where R is the reflectance of the surface after exposure, and R\(_0\) is the reflectance of the surface before exposure, i.e. background. The background spectrum was obtained from the bare polished copper surface before exposure. Some samples have very thick corrosion products. In this case, the corrosion products could be removed using a sharp knife. The spectra of the corrosion products could be obtained from transmission measurements using the KBr pellet method.

In order to identify the corrosion products, the spectra obtained from FTIR spectroscopy in the present thesis were compared with the reference spectra obtained from reference compounds in the author’s laboratory and the reference spectra reported in the literature\(^{55, 56, 78-83}\).

3.7 Experimental set-up for \textit{in situ} studies with FTIR microspectroscopy

\textit{In situ} surface analytical techniques are very important in mechanistic corrosion studies since they can provide information in real corrosive environments. Many surface analytical techniques, such as Auger electron spectroscopy, x-ray photoelectron spectroscopy and electron spectroscopy for chemical analysis, are based on electrons as probing particles and need high vacuum condition as a prerequisite, which makes them unsuitable for obtaining \textit{in situ} information on corrosion mechanisms. As a photon-based technique, Fourier transform infrared (FTIR) spectroscopy is a powerful technique to obtain information from thin films and monolayers on surfaces under \textit{in situ} conditions in humid gaseous environment
at ambient pressure. Several investigations have been accomplished to obtain *in situ* information of metal corrosion in humid air using Fourier transform infrared reflection absorption spectroscopy. There is no report on *in situ* measurements using Fourier transform infrared microspectroscopy (FTIR microspectroscopy). With the aid of microscope equipment, the physical development of the initial process and the whole corrosion process can be observed and *in situ* recorded by a video camera system. It turns out to be a powerful technique for *in situ* analysis of the corrosion products at different positions on a metal surface with a lateral resolution better than 50 μm. In the author’s laboratory, an experimental set-up based on *in situ* FTIR microspectroscopy measurements was recently developed and FTIR microspectroscopy was for the first time used for *in situ* studies in the field of atmospheric corrosion. Figure 6 shows a photo of the *in situ* FTIR microspectroscopy experimental set-up and a schematic picture of the *in situ* cell is shown in figure 7. The experimental cell is based on a modified transmission cell usually used for analysis of liquids. The metal sample was placed onto the surface of a rubber gasket isolating the metal sample from the metal holder of the *in situ* cell. A Teflon spacer was placed onto the surface of the metal sample. An IR-transparent window, made from ZnSe, was put onto the Teflon spacer so that a small space was formed over the metal sample. The distance between the IR window and the metal surface was about 1 mm, and the volume of the space about 250 mm$^3$. In order to avoid rupture of the IR window,
a Teflon spacer was put onto the surface of the IR window. Gas inlets and outlets allow humid air to pass through the in situ cell. The relative humidity and CO$_2$ concentration can be controlled in the in situ cell. After passage an oil filter, two particulate filters (3 and 0.01 µm, respectively), and a charcoal filter, the decontaminated laboratory pure air was divided into two streams. One humidified to 98-99% relative humidity and the other dry pure air. These two streams were then mixed in a chamber at different proportions to obtain the desired humidity, measured by a temperature/humidity sensor. The CO$_2$ concentration of the decontaminated pure air was below 5 ppm. To obtain a CO$_2$ concentration representative of ambient air (350 ppm), a small air-flow with CO$_2$ concentration of 2.5% was added from a CO$_2$ gas cylinder to control the CO$_2$ concentration in the cell, which can be calculated by the airflow flux, or by using the CO$_2$-analyzer. Gaseous pollutants (SO$_2$, NO$_2$ and O$_3$) can be introduced into the chamber at any desired concentration in the sub-ppm range. SO$_2$ was generated by permeation tubes and the concentration of SO$_2$ was analyzed with an SO$_2$-analyzer (Thermo Environmental 43C). The SO$_2$ analyzer was calibrated using the permeation rate and the gas flow rate, determined by weighing the permeation tube intermittently and by an air flow rate meter, respectively.

A NaCl particle, dimension of approximately (300-400)×(300-400)×(300-400) µm, was placed onto the central part of the metal sample before it was installed into the in situ cell. The airflow flux was kept constant at a flow rate along the surface of 300 ml/min. The temperature during exposure was 25±2°C. After about 10 minutes of exposure to clean dry air, humid air was introduced into the in situ cell. The
change of water absorption and corrosion processes could be observed and recorded by the microscope and spectra recorded in-situ by FTIR microspectroscopy. After exposure, the metal sample was taken out from the in situ cell and ex situ FTIR microspectroscopy was performed on the metal surface.

3.8 In situ and ex situ scanning Kelvin probe

Volta potentials were measured both in situ and ex situ using a commercial scanning Kelvin probe (UBM Messtechnik). The equipment was used to measure the distribution of the Volta potential on the sample surface and also the Volta potential changing with exposure time. The scanning Kelvin probe has an environmental chamber that enables in situ measurements to be performed at a controlled relative humidity. The probe was made from a Ni-Cr alloy and had a tip diameter of 50 µm. The surface topography of each sample was measured before the Volta potential distribution was recorded. This allowed the separation between the tip and the specimen to be kept constant during potential measurements and it was therefore possible to measure potentials on rough and rusted surfaces as well. The air gap between the probe and the sample was set to 50 µm. The lateral resolution of the probe was in the range of 80-100 µm. The vibration amplitude was 20 µm and the frequency 2 kHz. The probe potential was calibrated using a Cu/CuSO₄ redox system and it was re-calculated to the standard hydrogen electrode (SHE) scale. The samples were exposed to either air or argon at controlled relative humidity, which was monitored with a sensor located inside the environmental chamber. The temperature of the sample was set to 25°C. Changes in the work function of the probe turned out to be within 20 mV during wet/dry and during air/argon transitions after calibration. The potential measurements were carried out, and then repeated 1-2 hours later in order to ensure that the Volta potentials were not influenced by any static charging. The fact that the Volta potential did not change in magnitude to any significant degree during repetition showed that the static charging of NaCl crystals was negligible.
4. Summary of papers

In what follows, the main issues, observations and conclusions are summarized with reference to the corresponding papers.

4.1. Corrosion effects at relative humidities lower than the deliquescence point of the salt particles (Paper 1 and 6)

Significant corrosion effects were observed on NaCl and \((\text{NH}_4)_2\text{SO}_4\) deposited copper surfaces at relative humidities lower than the deliquescence point of particles. This is seen in figure 8 which shows the mass gain of copper exposed to humid air with 55% RH as a function of the amount of deposited NaCl particles and in figure 9 which shows the mass gain of copper exposed to 70% RH humid pure air vs the amount of deposited \((\text{NH}_4)_2\text{SO}_4\) particles (<10 µm). However, the corrosion effect was much lower at a relative humidity lower than the deliquescence point of particles (for NaCl around 75% RH and for \((\text{NH}_4)_2\text{SO}_4\) around 81% RH at 25 °C) compared to a humidity above the deliquescence point.

Figure 8. Mass gain of copper after 10 days of exposure to 55% RH and 25°C as a function of the amount of NaCl particles deposited.
Corrosion effects were observed both in the NaCl particle cluster and also in a circular zone of width 20 µm formed around the original deposited NaCl particle cluster, see figure 10. Cuprite was detected in the original NaCl particle cluster area and cuprite and copper carbonate were found in the circular zone outside the cluster. In the case of \((\text{NH}_4)_2\text{SO}_4\) particles, corrosion attack occurred at and close to the area of the deposited particles. Cuprite and antlerite are formed at the position of original deposited particles after exposure, see figure 11. The results show that NaCl and \((\text{NH}_4)_2\text{SO}_4\) particles induce a significant acceleration of the corrosion rate of copper even at relative humidity well below the deliquescence point of deposited particles. At 55% RH, only about 2-3 monolayers of water adsorb onto a copper surface in the absence of NaCl particles, corresponding to a mass gain of approximately 0.06-0.09 µg/cm\(^2\) \(^{51}\). At 70% RH, about five monolayers of water adsorb onto a copper surface in the absence of \((\text{NH}_4)_2\text{SO}_4\), corresponding to a mass gain of approximately 0.15 µg/cm\(^2\) \(^{51}\). There is not enough absorbed water to dissolve the particles at the relative humidity lower than the deliquescence point of deposited particles. However, it is possible that enough water is retained in micro-cracks, crevices and other more occluded volumes of the NaCl and \((\text{NH}_4)_2\text{SO}_4\) particle cluster. Small amounts of ions could dissolve from the NaCl and
Figure 10. SEM micrograph (a) and FTIR microspectra (b) obtained at different locations of copper with 4 µg/cm² NaCl particles added and after 10 days of exposure to 55% RH.

Figure 11. FTIR microspectra obtained on the original particles cluster before (A) and after 1 minute (B) of washing in clean water. Transmission spectrum of antlerite, Cu₃(OH)₄SO₄, was shown as a reference spectrum. (10 days of exposure to 70% RH and 350 ppm CO₂)
(NH₄)₂SO₄ particles and react with copper. Only localised dissolution of copper at the original particles deposit area occurred since the amount of water absorbed is very small and the solution can not spread over the whole surface.

4.2 The secondary spreading effect from electrolyte droplet (Paper 3, 5 and 7)

The secondary spreading effect from the peripheral part of NaCl droplets on copper surfaces was studied using different in situ techniques. A copper surface was deposited with a single NaCl particle and then exposed to 80% RH humid pure air with two concentrations of CO₂ (<5 and 350 ppm). Upon introduction of humid air (80% RH), the pre-deposited NaCl particle was transformed into an electrolyte droplet. Outside the droplet a thin electrolyte film was formed, caused by secondary spreading from the original droplet. Figure 12 shows an in situ optical micrograph of a copper surface deposited with a NaCl particle after 1 hour of exposure to pure air with 80% RH and < 5 ppm CO₂. A secondary spreading area was clearly seen on the peripheral part of the electrolyte droplet. Ambient level of CO₂ (350 ppm) resulted in a relatively low secondary spreading effect, whereas the lower level of CO₂ (<5 ppm) caused a much faster secondary spreading effect over a large area. The secondary spreading effect is mainly due to changes in surface energy of the metal oxide surface close to the periphery of the droplet. These

Figure 12. In situ optical micrograph of a copper surface deposited with a NaCl particle after 1 hour of exposure to pure air with 80% RH and < 5 ppm CO₂.
changes are consequences of the separation of oxygen reduction, taking place at the periphery of the droplet, and the anodic metal dissolution in the central part of the droplet. The large secondary spreading at low CO₂ concentration is due to larger changes in the surface tension at the electrolyte/oxide interface due to the very alkaline pH created in the cathodic areas at the low CO₂ concentration. The continuous growth of the secondary spreading area at low CO₂ concentration is possible due to the galvanic coupling with the droplet leading to transport of sodium ions to the cathodic region and maintenance of the alkaline conditions. The alkaline conditions in the secondary spreading area were evidenced from the in situ measurements and were due to the cathodic oxygen reduction in the secondary spreading area. In situ scanning Kelvin probe measurements also showed that the cathodic reactions took place in the secondary spreading area, leading to a very high pH there. The geometrical profile of the measured area (A) and the corresponding Volta potential profile (B), at and close to the water droplet, after 0.5 and 3 hours of exposure to humid air with <5 ppm CO₂ are shown in figure 13.

Figure 13. Geometrical profile (A) and Volta potential (V) distribution (B) of a copper surface at and close to the water droplet after 0.5 and 3 hours of exposure to 85% RH and low CO₂ concentration (<5 ppm).
The water droplet of electrolyte formed around the NaCl crystal is located at the left-hand side of the plots. The potential under the water droplet is approximately 150 mV lower relative to the surrounding copper surface, due to activation of the anodic dissolution of copper under the droplet. After 3 hours exposure time, a separation of the Volta potential into three different areas is clearly visible. The first area corresponds roughly to the droplet as seen from the geometrical profile. The second area is outside this area and the potential increases 50-60 mV relative to the potential in the first area. The third area is the copper surface outside the second area with a potential 150 mV higher than the area under the droplet. The steep increase in the potential between the second and the third area marks the front of the advancing cathode as the electrolyte layer spreads on the surface. In the second area, oxygen reduction takes place and also, to some extent, anodic dissolution of copper due to the alkaline conditions. At 350 ppm CO₂, carbonate formation in the secondary spreading area results in lowering of the pH. This increases the surface tension of the oxide/electrolyte interface and inhibits the secondary spreading. Figure 14 shows optical micrographs of copper surfaces deposited with a NaCl particle after 6 hours of exposure to 80% RH humid pure air with 350 ppm or <5 ppm CO₂. As the results show in figure 14, the secondary spreading area at <5 ppm CO₂ is much larger than that at 350 ppm CO₂.

![Figure 14. Optical micrographs of copper surfaces deposited with a NaCl particle after 6 hours of exposure to 80±2% RH and 350 ppm or <5 ppm CO₂.](image)

After introduction of SO₂ into the exposure chamber the secondary spreading ceased. SO₂ dissolved into the cathodic area around the water droplet and picked up water to form hydrated sulfur dioxide. This decreased the pH in the secondary
spreading area and prevents the spreading of the electrolyte. The deposition of SO$_2$ is promoted by the high pH in the secondary spreading area.

![Micrographs](image)

Figure 15. Optical micrographs of zinc surfaces deposited with a NaCl particle after 6 hours of exposure to 90% RH and 350 ppm or <5 ppm CO$_2$.

Similar results were observed on zinc surfaces. Figure 15 shows optical micrographs of zinc surfaces deposited with a NaCl particle after 6 hours of exposure to 90% RH pure air with 350 ppm or <5 ppm CO$_2$. As seen in figure 15, the secondary spreading area at <5 ppm CO$_2$ is much larger than that at 350 ppm CO$_2$.

In the presence of SO$_2$ a small secondary spreading effect of the NaCl electrolyte on copper was observed, whereas no secondary spreading effect on zinc surface could be seen. No secondary spreading effect of (NH$_4$)$_2$SO$_4$ electrolyte was ever observed.

### 4.3 NaCl particle induced atmospheric corrosion of copper in humid air – the role of CO$_2$ (Paper 4)

The corrosion rates and the composition and distribution of corrosion products were investigated after exposure of NaCl deposited copper surfaces to humid air. With lower amount of NaCl particles on the copper surface (<15 µg/cm$^2$), the corrosion rate was higher with <1 ppm CO$_2$ than with 350 ppm CO$_2$, but with higher amount of NaCl (>15 µg/cm$^2$), the corrosion was higher with 350 ppm CO$_2$. This can be explained by the secondary spreading effect from the NaCl electrolyte droplets, which leads to the formation of a larger effective cathodic area and increases the corrosion rate under these conditions. At 350 ppm CO$_2$, there is no large secondary spreading area outside the NaCl droplets and the effective cathodic area will not increase with time. As the surface density of NaCl particles increases,
the secondary spreading areas from the particles will overlap and the increase of the effective cathodic area can not continue. Thus, at higher NaCl particle density the difference in effective cathodic area is small between low (<1 ppm) and high (350 ppm) CO₂ concentration. For low CO₂ concentration, the NaCl induced corrosion led to the formation of corrosion products containing Cu₂O, CuO, Cu₂(OH)₃Cl, Cu(OH)₂, and CO₃²⁻. The high pH value in the surface electrolyte at <1 ppm CO₂ promoted the formation of CuO. This increased the corrosion resistance of the corrosion product layer and contributed to a lower corrosion rate at <1 ppm CO₂ at higher surface concentration of NaCl. At 350 ppm CO₂, the corrosion products after exposure include Cu₂O, Cu₂(OH)₂CO₃, CO₃²⁻ and Cu₂(OH)₃Cl. Another important factor is the amount of soluble chloride at <1 ppm CO₂. Less chloride ions are bonded in insoluble corrosion products and can contribute to a more localised corrosion and a higher corrosion rate in this case. Figure 16 shows a

![Figure 16](image-url)
schematic picture of the corrosion product layer formation during exposure of copper to humid pure air with <1 and 350 ppm CO$_2$. Figure 17 summarizes the effect of CO$_2$ on the NaCl induced corrosion of copper.

![Diagram of CO$_2$ concentration effects on NaCl-induced copper corrosion](image)

Figure 17. Summary of the effect of CO$_2$ on the NaCl-induced atmospheric corrosion of copper.

### 4.4 The role of NaCl particles on the atmospheric corrosion of copper in humid air containing SO$_2$ (Paper 2 and 5)

The role of NaCl particles on the initial atmospheric corrosion of copper in humid air containing SO$_2$ was examined with FTIR microspectroscopy under in situ and ex situ conditions in order to reveal the spatial distribution of reaction products. The copper surface was deposited with a single NaCl particle and then exposed to air with 80% RH and 150 ppb SO$_2$ and with either ambient CO$_2$ level (350 ppm) or low CO$_2$ level (<5 ppm). In the presence of SO$_2$, a small secondary spreading effect
of electrolyte from the edge of the droplet was observed. The oxidation of S(IV) turns out to be fast at the area of the NaCl-containing electrolyte droplet, and both sulfate ($SO_4^{2-}$) and dithionate ($S_2O_6^{2-}$) ions form. A copper catalysed reaction route

**Figure 18.** Schematic illustration of important processes in the water droplets on a copper surface during initial exposure and the corrosion products formed after 24 hours of exposure (150 ppb $SO_2$, 80% RH).
for the sulfite oxidation was suggested which includes the formation of a Cu(II)–sulfito complex as an important step. The presence of gaseous oxidants such as NO₂ and O₃ has previously been considered as an important prerequisite for the oxidation of sulfite on copper. The results obtained here suggest that the formation of local electrochemical cells induced by deposited NaCl particles, whose anode mainly occurred under the droplet and cathode mainly occurred in the secondary spreading area, could be another important route for S(IV)-oxidation to sulfate. SO₂ was found to promote the formation of less soluble corrosion products. The electrolyte droplet was dried after 24 hours of exposure due to the formation of less soluble paratacamite (Cu₂(OH)₃Cl) and nantokite (CuCl), whereas the electrolyte droplet did not dry even after 48 hours of exposure to environments in the absence of SO₂. The corrosion products formed in the area of the electrolyte droplet are nantokite (CuCl), paratacamite (Cu₂(OH)₃Cl), sulfate, and small amounts of dithionate and carbonate (CO₃²⁻). The corrosion products formed in the secondary spreading area are sulfite with small amounts of sulfate and dithionate. Figure 18 is a schematic description of important observations and conclusions related to the effect of SO₂ on the NaCl-induced atmospheric corrosion of copper under current exposure conditions. As the results show in Paper 2, the mass gain of copper deposited with NaCl particles exposed in SO₂-containing humid air is lower than that exposed in humid pure air. It is probably due to the decrease of soluble chloride in the reaction products formed. This will lead to a decrease in the electrolyte thickness in the presence of SO₂ after longer time (>24 hours) of exposure and a decrease in the corrosion rate. Hence, whereas SO₂ alone promotes the corrosion rate, in the presence of NaCl particles the corrosion rate may slow down due to the formation of more insoluble copper chloride compounds.

4.5 The role of NaCl particles on the atmospheric corrosion of zinc and the effect of CO₂ and SO₂ (Paper 7)

Figure 19 shows mass loss of zinc, after 10 days of laboratory exposure in 90% RH pure air with <1 or 350 ppm CO₂, as a function of the amount of deposited NaCl particles. As the results show in figure 19, the mass loss at <1 ppm CO₂ is higher than at 350 ppm CO₂ with the same amount of deposition of NaCl particles. Results from ion chromatography measurements show that the amount of water-soluble chlorides in the corrosion products formed after exposure at <1 ppm CO₂ is much higher than that in the corrosion products formed after exposure at 350 ppm CO₂. In order to obtain more insight into the mechanisms of the NaCl particle induced corrosion of zinc, the corrosion process was studied using FTIR microspectroscopy under in situ and ex situ conditions. The zinc surface was deposited with a single
NaCl particle and then exposed to 90% RH air with two concentrations of CO$_2$ (<5 and 350 ppm) and SO$_2$ (0 and 250 ppb), respectively. Figure 20 summarizes the important observations and conclusions related to NaCl-induced atmospheric corrosion of zinc under current exposure conditions. Upon introduction of humid air (90% RH) the pre-deposited NaCl particle was transformed into an electrolyte droplet. Outside the droplet a thin electrolyte film was formed, caused by secondary spreading from the original droplet. Ambient level of CO$_2$ (350 ppm) resulted in a relatively low secondary spreading effect, whereas the low level of CO$_2$ (<5 ppm) caused a significant secondary spreading over a large area, see figure 20 upper and middle part. In addition, many smaller micro-droplets formed in the secondary spreading area. Chloride was concentrated in the micro-droplets in the secondary spreading area. However, more cations moved into the secondary area than anions. Different secondary spreading behaviour and pH affect the corrosion processes, such as the cathodic areas, the formation of corrosion products and water-soluble chloride left in the corrosion products. Larger cathodic area, higher amount of water-soluble chloride left in the corrosion products and formation of ZnO at <5 ppm CO$_2$ induced higher corrosion rate at <5 ppm CO$_2$ than at 350 ppm CO$_2$. An important finding is the proportion between anodic and cathodic areas after exposure. These areas could be identified by the phases

Figure 19. Mass loss of zinc, deposited with different amount of NaCl particles, after 10 days of exposure to 90% RH.
Figure 20. Schematic illustration of the NaCl-induced atmospheric corrosion of zinc in humid air of different composition. Upper: <5 ppm CO₂; middle: 350 ppm CO₂; lower: 250 ppb SO₂.
associated with each area through *in situ* FTIR microspectroscopy. Phases that may occur at the central anodic area are simonkolleite \((\text{Zn}_5\text{(OH)}_8\text{Cl}_2\cdot\text{H}_2\text{O})\), zincite \((\text{ZnO})\) and hydrozincite \((\text{Zn}_5\text{(OH)}_6\text{(CO}_3)_2)\), whereas the main phase that occurs in the peripheral cathodic area is sodium carbonate \((\text{Na}_2\text{CO}_3)\). At <5 ppm CO₂, the anodic area was much smaller than that at 350 ppm CO₂, while the cathodic area at <5 ppm CO₂ is much larger than that at 350 ppm CO₂. As a result of the different anode to cathode area ratios, more localized corrosion was observed at <5 ppm CO₂, whereas more general corrosion was observed at 350 ppm CO₂. Figure 21 summarises the different effects of CO₂ on the NaCl induced corrosion of zinc. In the presence of SO₂, CO₂ did not affect the corrosion process and no secondary spreading effect was observed, see figure 20 lower part. An important finding is the influence of NaCl on the oxidation of S(IV) to S(VI). The oxidation of SO₂ to sulfate is much faster in the presence than in the absence of NaCl particles and the fast oxidation of SO₂ to sulfate occurs in the electrolyte droplet, probably as a result of a surface \((\text{ZnO})\) mediated catalytic process.

![Diagram](image)

**Figure 21.** Summary of the effect of CO₂ on the NaCl-induced atmospheric corrosion of zinc.

35
4.6 The role of $(\text{NH}_4)_2\text{SO}_4$ particles on the atmospheric corrosion of copper in humid pure air (Paper 6)

In the present study, a simple and effective way was found to deposit the $(\text{NH}_4)_2\text{SO}_4$ particles and separating the particle size distributions into smaller and larger. Deposition of smaller particles resulted in evenly distributed particles with size of approximately $<10\ \mu\text{m}$. On the other hand, deposition of larger particles resulted in less evenly distributed particles with size of approximately $<100\ \mu\text{m}$. After exposure to humid air, cuprite and basic copper sulfate were detected on the copper surfaces. The effect of the $(\text{NH}_4)_2\text{SO}_4$ particle size on corrosion rate was investigated and figure 22 shows the mass gains of copper samples, deposited with different amount of $(\text{NH}_4)_2\text{SO}_4$ particles with size $<10\ \mu\text{m}$ or $<100\ \mu\text{m}$, and after 10 days of exposure. The mass gain increases with the amount of added $(\text{NH}_4)_2\text{SO}_4$ particles in the studied range. The size of particles affects the corrosion rate; smaller particles resulted in a higher corrosion rate than larger particles at equal amount of deposition. This effect can be explained by the higher surface coverage of the smaller particles. Mass gain and mass loss of copper with $(\text{NH}_4)_2\text{SO}_4$ particles increased with exposure time. The formation of $\text{Cu}_2\text{O}$ was the main corrosion attack after longer than 10 days of exposure. The growth of $\text{Cu}_2\text{O}$ was promoted by the formation of a porous oxide structure and a catalytic reaction sequence involving $\text{NH}_3$.

![Figure 22](image_url)  
Figure 22. Mass gain of copper, deposited with different amount of $(\text{NH}_4)_2\text{SO}_4$ particles, after 10 days of exposure to 90% RH and 350 ppm CO$_2$. The deposited particle size is smaller ($<10\ \mu\text{m}$) or larger ($<100\ \mu\text{m}$).
4.7 Comparison of the corrosion effect of NaCl and (NH$_4$)$_2$SO$_4$ particles on copper and zinc (Paper 4 and 6)

Figure 23 shows mass loss of copper deposited with (NH$_4$)$_2$SO$_4$ or NaCl particles after 10 days of exposure to humid pure air with 350 ppm CO$_2$. The corrosion of copper induced by (NH$_4$)$_2$SO$_4$ particles is much higher than that of NaCl particles. While, the corrosion rate of zinc in the presence of (NH$_4$)$_2$SO$_4$ particles is much lower than that induced by NaCl particles, as seen in figure 24.$^{73}$

The difference between copper and zinc is directly related to the differences in the corrosion mechanism for these metals. The reaction of copper with (NH$_4$)$_2$SO$_4$ particles may lead to the formation of cuprite, catalyzed by NH$_3$. The formation of a porous cuprite layer is observed over a larger part of the copper surface and the NH$_3$ catalysed formation occurs in the porous structure growing on the surface. The amount of cuprite formed on copper, deposited with NaCl particles, is much lower than of copper deposited with (NH$_4$)$_2$SO$_4$ particles. For zinc, the mechanism is different and the sulfate ions combine stochiometrically with zinc to form an insoluble basic sulfate.$^{73}$ Once the (NH$_4$)$_2$SO$_4$ has been consumed the corrosion ceases.

Figure 23. Mass loss of copper after 10 days of exposure to humid air with 350 ppm CO$_2$. The results from (NH$_4$)$_2$SO$_4$ particles are at 90% RH. The results from NaCl particles are at 85% RH.
Figure 24. Mass loss of zinc, deposited with different amount of particles, after 10 days of exposure to 90% RH and 350 ppm CO$_2$. 

![Graph showing mass loss of zinc with different amounts of deposited particles]
5. Conclusions

In this thesis the initial particle (NaCl or (NH₄)₂SO₄) induced atmospheric corrosion of copper and zinc has been investigated under *in situ* and *ex situ* conditions using a newly developed technique – *in situ* FTIR microspectroscopy. In addition, complementary analysis has been performed by means of microgravimetry, FTIR spectroscopy, ion chromatography, scanning electron microscopy with x-ray microanalysis and the scanning Kelvin probe. The composition and lateral distribution of corrosion products on the surfaces were determined, and the results discussed in view of different mechanisms of the particle induced corrosion.

The following main conclusions have been drawn:

1. The composition and spatial distribution of corrosion products is governed by the location of the anodic and cathodic sites, the transport of ions and other species between these sites, and the deposition of gases on the surface.

2. A surface tension driven secondary spreading effect was observed from NaCl droplets on copper and zinc surfaces. This effect is strongly dependent on the CO₂ content, and reduced level of CO₂ (<5 ppm) results in a much faster secondary spreading effect over a large area compared to ambient level of CO₂ (350 ppm). In the former case alkaline conditions prevail in the cathodic area, leading to large changes in the surface tension at the oxide/electrolyte interface in the peripherical parts of the droplet. A surface tension driven convective flow of electrolyte is induced from the NaCl droplet. Galvanic coupling between the peripheral surface part and the inner surface part of the droplet leads to transport of sodium ions to peripheral parts and maintenance of alkaline conditions there, whereby a continuous growth of the secondary spreading area at low CO₂ concentration occurs. At 350 ppm CO₂, carbonate formation in the secondary spreading area results in lowering of the pH. This increases the surface tension of the oxide/electrolyte interface and inhibits the secondary spreading effect.

3. CO₂ strongly affects the NaCl-induced atmospheric corrosion of copper and zinc. For copper several independent mechanisms have been identified. CO₂ affects the secondary spreading behaviour of the electrolyte droplet and pH value of the electrolyte. Different secondary spreading behaviour and pH affect the corrosion processes, such as the cathodic areas, the formation of corrosion products and water-soluble chloride left in the corrosion products. Larger cathodic area (due to
the secondary spreading effect), higher amount of water-soluble chloride left in the corrosion products and formation of CuO on copper at <5 ppm CO₂ results in higher corrosion rates at lower NaCl particle density. At higher NaCl particle density, the secondary spreading areas from the particles overlap and no increase in the effective cathodic area is possible. In this situation, the corrosion rate is higher at ambient CO₂ concentration, since more protective CuO-containing corrosion products are formed at low CO₂ concentration.

4. Sulfite (SO₃²⁻) oxidation and sulfate (SO₄²⁻) formation on copper is promoted by the formation of galvanic elements within the NaCl-containing electrolyte droplet. For the first time, evidence for the formation of dithionate (S₂O₆²⁻) was also found during an atmospheric corrosion process, and a copper catalyzed reaction route for the sulfite oxidation was suggested. The formation of a Cu(II)–sulfito complex in the droplet electrolyte is probably a crucial step in the oxidation reaction sequence of SO₃²⁻ on copper surfaces. Paratacamite (Cu₂(OH)₃Cl) and nantokite (CuCl) formation were both promoted by the SO₂ deposition. SO₂ alone promotes the corrosion rate of copper, but in the presence of NaCl particles the corrosion rate of copper may slow down due to the formation of these more insoluble copper chloride compounds.

5. The oxidation of SO₂ to sulfate on zinc is also promoted by NaCl. In the presence of NaCl particles, only sulfate, and no sulfite, is formed in the electrolyte droplet area after exposure. In the absence of NaCl particles, sulfite is the main product. For zinc, the sulfite oxidation process is probably catalysed by the formation of a sulfito-surface complex on ZnO particles, which results in rapid formation of sulfate in the electrolyte droplet area.

6. Simple and effective methods have been found to deposit NaCl and (NH₄)₂SO₄ particles on the metals investigated. Deposition of NaCl results in evenly distributed circular particle clusters with diameters of approximately 100 µm. The clusters consist of individual NaCl particles of size less than 10 µm. Deposition of (NH₄)₂SO₄ particles under the conditions described here, results in evenly distributed particles with size of lower than 10 and 100 µm, respectively.

7. Significant corrosion attack at relative humidity lower than the respective deliquescence point was observed, both on NaCl and (NH₄)₂SO₄ deposited copper surfaces.
8. Cuprite (Cu$_2$O) and basic copper sulfate have been detected on copper deposited with (NH$_4$)$_2$SO$_4$ particles after exposure to humid pure air. The size of particles affects the corrosion rate. Smaller particles result in a higher corrosion rate than larger particles at equal amounts of deposition, due to high surface coverage of the smaller particles. Mass gain and mass loss of copper deposited with (NH$_4$)$_2$SO$_4$ increase with exposure time. The formation of cuprite was the main corrosion attack after longer exposures than 10 days. The enhanced cuprite formation on copper could be explained by a reaction sequence catalysed by NH$_3$.

9. On copper, (NH$_4$)$_2$SO$_4$ particles are more corrosive than NaCl particles, whereas on zinc, the opposite has been found. This can be explained by different corrosion mechanisms operating on copper and zinc, respectively.
6. Acknowledgements

I would like to express my sincere gratitude to Prof. Christofer Leygraf. Thank you very much for inviting me and giving me the opportunity to join this nice group in Sweden. I sincerely thank you for all your support, and for generously, imparting your knowledge, enthusiasm and ideas to me. You are great and thank you very much!

Dr. Dan Persson is gratefully acknowledged for continuous encouragement and support, both professionally and privately. You gave me great patience and understanding. I appreciate all time and the support from you. Thanks a lot to your scientific questions, discussions and improvements of the papers.

Thanks to Dr. Saeid Zakipour, for continuous encouragement and support. I appreciate all the time and the support from you.

I would like to thank Dr. Johan Tidblad and Docent Dr. Dominique Thierry for your valuable discussions and suggestions. I sincerely thank you for your helps and support to my research.

I would like to thank Prof. Yuanlong Du, in the Metal Research Institute, Chinese Academy of Sciences, for your support and encouragement of my work here.

I would like to thank the whole staff of the Swedish Corrosion Institute, who created a very nice environment for scientific research and helped me in many ways. The following deserve special thanks:
Kaija Eistrat for helping in the library.
Vladimir Kucera for helpful discussions and suggestions.
Andrej Nazarov for helping with the scanning Kelvin probe experiments.
Kenneth Göransson for helping to solve the computer problems.
Farid Samie for helping with ion chromatography experiments.
Helen Pahverk for making the synthesis of some compounds.

Sincere thanks also for help from assistant Prof. Inger Odnevall for providing me some useful reference papers about atmospheric corrosion of zinc.

Thanks a lot to assistant Prof. Jinshan Pan and his wife, Dr. Wenle He. Thank you for your encouragement.
Prof. Zhizhong Ma, Prof. Meiqi Ye and M.Sc. Yan Zhuang, in Xiamen Branch Department of Luoyang Ship Material Research Institute, China, are all acknowledged for your support, encouragement and kind help. Other staff members of this institute are also appreciated for their support.

I would like to thank my Chinese friends Guangyu Sun, Jiazhen Hu and Qian Dong for the happy life together in Stockholm. Thank you for the good friendship and for your kind support, encouragement and help.

Finally, I wish to thank my big family in China for their love, sacrifices and moral support during the course of this work. Especially, I would like to express my sincere thanks to my great mother, Yueying Huang (黄月英), my kind-hearted father, Songlin Chen (陈松林) and my beloved wife, Guiying Tian (田桂英). Thank you very much!

Zhuoyuan Chen (陈卓元)

7. References

52. P. V. Strekalov, V. V. Agafonov and Y. N. Mikhailovski, Protection of Metals, 8, 521-523, 1972
57. Z. Y. Chen, D. Persson and C. Leygraf, Initial NaCl Particle Induced Atmospheric Corrosion of Zinc- Effect of CO2 and SO2, Manuscript
69. H. Kaesche, Werkstoffe und Korrosion, 15, 379 (1964)
73. Z. Y. Chen, D. Persson and C. Leygraf, The Effect of NaCl and (NH₄)₂SO₄ Particles on the Atmospheric Corrosion of Zinc, manuscript
83. Z. Y. Chen, S. Zakipour, D. Persson and C. Leygraf, The Combined Effects of Gaseous pollutants and Sodium Chloride Particles on the Atmospheric Corrosion of Pure Copper, Corrosion, accepted for publication