Corrosion initiation induced by sodium sulfate and sodium chloride particles on Cu and the golden alloy Cu5Al5Zn at simulated atmospheric conditions

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Abstract

Effects of sodium sulfate (Na$_2$SO$_4$) particle deposition on the atmospheric corrosion of copper (Cu) metal and a Cu-based alloy (Cu5Al5Zn) used in architectural applications were investigated at laboratory conditions compared with effects induced by sodium chloride (NaCl) and to some extent ammonium sulfate (NH$_4$)$_2$SO$_4$ induced corrosion. Pre-deposited surfaces were exposed to repeated wet/dry conditions in a climatic chamber and the formation of corrosion products were assessed using light optical microscopy (LOM), scanning electron microscopy with elemental analysis (SEM/EDS), Fourier transform infrared techniques (FTIR microscopy) and cathodic reduction (CR). Na$_2$SO$_4$ induced corrosion resulted in corrosion cells locally over the surface on both Cu and Cu5Al5Zn, of increased oxygen content in the anodic area of the cells (center of pre-deposited area). The main corrosion products formed on Cu metal are basic copper sulfates and cuprite (Cu$_2$O), while basic sulfates (copper and/or zinc) and Cu$_2$O were the main corrosion products formed on Cu5Al5Zn. A combined deposition of Na$_2$SO$_4$ + NaCl was carried out on the Cu5Al5Zn alloy using two different deposition methods to investigate the possible interplay from a corrosion initiation perspective between the two salt particles. For short time exposed Cu5Al5Zn (1 cycle), two different corrosion cells formed, mainly induced by Na$_2$SO$_4$ and NaCl. Corrosion products formed in anodic areas of a Na$_2$SO$_4$ induced corrosion cell were similar to findings observed for Cu5Al5Zn pre-deposited with Na$_2$SO$_4$ only, whereas peripheral cathodic areas primarily were affected by NaCl dissolution and predominantly composed of Cu$_2$O that was the main corrosion product with small amount of hydroxides and carbonates of the NaCl induced corrosion cells. After relatively longer exposure periods (2 and 6 wet/dry cycles), NaCl dominated the corrosion of the entire surface with the formation of more Cu$_2$O, hydroxides and carbonates. Cathodic reduction findings revealed a negative interplay on corrosion for the mixed salt after short time exposures (1 and 2 cycles), whereas a slight synergistic effect was evident after a longer exposure period (6 cycles), compared with corrosion induced by single salts.

Keywords: atmospheric corrosion, Na$_2$SO$_4$, NaCl, Cu5Al5Zn, Cu metal, mixed salt pre-deposition, laboratory exposure, LOM, SEM/EDS, ATR-FTIR, cathodic reduction.
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1. Introduction
1.1 Motivation and objectives
Atmospheric corrosion of Cu metal is extensively investigated by many scientists, including effects of gaseous and particulate pollutants deposition at laboratory exposures and field exposures at different environmental sites. For particle deposition on Cu surfaces, NaCl and (NH₄)₂SO₄ are the most investigated particles that have been investigated during the past decades by e.g. Chen et al. [1] and Lobnig et al. [2,3] Na₂SO₄, which is also abundant in coastal and urban environments, is less extensively studied. The aim of this project is to improve the knowledge and understanding of the influence of Na₂SO₄ deposition on Cu metal and Cu5Al5Zn surfaces under cyclic laboratory exposures and compare its corrosive effects with corresponding effects of NaCl, in particular, and to some extent also with (NH₄)₂SO₄.

The Cu5Al5Zn alloy is lately widely used in architectural construction due to its beneficial corrosion properties and aesthetic appearance. Its prevailing atmospheric corrosion mechanisms are though poorly understood. Since previous investigations [4] on the Cu5Al5Zn alloy predominantly have focused on its corrosion performance in chloride-rich atmospheres, this study has focused on the effect of Na₂SO₄ deposition on the Cu5Al5Zn alloy, compared with results on Cu metal.

Moreover, to mimic the real-life condition at for instance a coastal environment, a combined salt deposition of NaCl and Na₂SO₄ was carried out to investigate its corrosion effects, aspects not previously studied. Procedures for salt deposition were elaborated by means of two different methods. These surfaces were exposed to repeated cyclic wet and dry conditions in a climatic chamber at constant temperature and different relative humidity (RH) levels. After exposure, information was obtained on the formation of different corrosion cells induced by different salt crystals and whether synergistic effects between crystals of the two different salts could be observed. The interplay between the deposition of the two salts was compared with parallel measurements using single salt deposition by means of cathodic reduction.

Even though the laboratory exposure accelerated reactions that take place at field conditions, the investigations of this study predominantly focused on corrosion initiation. As a consequence, most corrosion products formed were in their amorphous states and the rate of corrosion was not terminated within the investigated exposure periods (days and weeks).

A multi-analytical approach was conducted using the following techniques to assess the extent and composition of corrosion product formation on Cu metal and the Cu5Zn5Al alloy. Light Optical Microscopy (LOM) and Scanning Electron Microscopy (SEM) were used to determine the surface morphology and topography of corroded samples. Energy Dispersive X-ray Spectroscopy (EDS), Attenuated Total internal Reflectance Fourier Transform Infrared spectroscopy (ATR-FTIR) and Grazing Incidence X-ray Diffraction (GIXRD) were employed to assess corrosion products and functional groups. Electrochemical Cathodic Reduction (CR) was performed to predict differences in patina thickness of corrosion products formed on the surface by applying a constant current.
1.2 Sustainability aspect
The project contributes to the Sustainable Development Goal (SDGs) No. 9, Build resilient infrastructure, that promotes sustainable industrialization and foster innovation. The atmospheric corrosion of Cu and Cu-based alloys is of great interest to investigate since metals are widely used in outdoor construction, for example, as cladding and façades of buildings. An improved understanding of underlying mechanisms of atmospheric corrosion at different exposure conditions enable possibilities for sustainable use of metals, which result in better performance and long-term service life.
2. Literature survey

2.1 Atmospheric corrosion

Atmospheric corrosion, one of the most important corrosion processes, is defined as the interaction between the ambient environment and the objective material, mostly a metal, and involves chemical, electrochemical, and physical processes. It is complex since these processes take place within a system, including three phases and two interfaces, one between the gaseous and the liquid (aqueous layer) and the other between the aqueous layer and the solid (the metal surface, usually with a surface oxide) \(^6\). The science of atmospheric corrosion was pioneered by Vernon around a century ago, who for instance discovered that the corrosion process is rapidly accelerated beyond a “critical humidity” and that pollutants such as SO\(_2\) and particle aerosols influence the corrosion process \(^7\). At atmospheric corrosion, a thin aqueous layer is formed via rapid hydroxylated reactions on the metal surface as a result of the relative humidity (RH) level in the ambient atmosphere \(^6\). This water layer may vary from monomolecular thickness to visible water films as a result of different humidity conditions, for example, a relative humidity of 20% typically leads to a water layer of monolayer thickness on the surface while 75% results in a five times thicker layer \(^8\). The relative humidity is defined as the ratio between the absolute humidity and the saturated water quantity \(^9\). RH significantly fluctuates with the climatic variations over the day with temperature change, leading to a variation in the aqueous layer thickness due to repeated dry and wet conditions. This is vital for the atmospheric corrosion process because the water layer not only acts a medium for electrochemical and chemical reactions but also as a solvent for other constituents \(^6\). Figure 2.1 schematically shows different regimes involved in atmospheric corrosion.

![Figure 2.1 Different regimes involved in atmospheric corrosion.](image)

Atmospheric constituents, gaseous pollutants and airborne salt particles dissolve and deposit in the aqueous adlayer, resulting in series of interfacial chemical and electrochemical reactions \(^6\). At low relative humidity, the water droplets form unevenly on the surface instead of as a water layer. This leads to local electrochemical corrosion cells with separate anodic and cathodic parts. Most electrochemical reactions take place with anodic oxidization and cathodic reduction, general equations given below:
Dissolved metal ions combine with counterions present in the aqueous layer to precipitate into different solid phases (corrosion products) when the ion pairs reach supersaturation in the aqueous layer. In the final stage of atmospheric corrosion, the precipitated nuclei grows with prolonged exposure, eventually leading to a complete surface coverage of corrosion products.

2.2 Gaseous and particulate pollutants

Important gaseous pollutants such as nitrogen dioxide (NO₂), sulfur dioxide (SO₂), hydrogen chloride (HCl), hydrogen sulfide (H₂S), carbon dioxide (CO₂), ammonia (NH₃), nitric acid (HNO₃), oxygen (O₂), ozone (O₃), hydrogen peroxide (H₂O₂), and formaldehyde (HCHO) all have a great influence of atmospheric corrosion. Recent two decades from 1990, the emissions of gaseous pollutants, especially for SO₂ and NOₓ (NO+NO₂), have decreased drastically in many countries, such as in Europe and North America. Thus, corrosion effects induced by airborne salt particles, for example, sodium chloride (NaCl), ammonium sulfates ((NH₄)₂SO₄, NH₄HSO₄), ammonium chloride (NH₄Cl), and sodium sulfate (Na₂SO₄), abundant pollutants in marine environment and urban atmosphere become more important.

Figure 2.2 illustrates how atmospheric corrosion can be induced by airborne salt particles at a given relative humidity. To elucidate these processes, the concept of deliquescence should be explained first. Deliquescence is a process that follows from when a substance absorbs the moisture in the atmosphere and becomes initially partially dissolved and finally forms a solution when the relative humidity is high enough at a given temperature. All salts will be deliquescent at a certain relative humidity (depending on temperature), a RH denoted as the point of deliquescence. A substance that absorbs moisture from the atmosphere but does not necessarily dissolves entirely is called hygroscopic. Both of the situations could induce atmospheric corrosion, e.g. when different salt particles become deposited on a metal surface. Deliquescence points are temperature dependent and also influenced by other factors, for example, size of particles, and interplay with other particles.

An aqueous layer is formed on all metal surfaces exposed to an environment. Gaseous pollutants and airborne salt particles from the atmosphere deposit on the surface and dissolve, or partially dissolve, in
the aqueous layer. This layer acts as electrolyte in which chemical reactions take place and electrochemical reactions occur on the metal that acts as the anode. Cathodic reactions take place with oxygen reduction [6].

Corrosion effects induced by chlorides at atmospheric conditions for copper (Cu) and Cu-based alloys under different exposure conditions are extensively investigated in the scientific literature, e.g. by depositing NaCl crystals at laboratory exposure conditions or at field conditions [4,12–17]. The chloride-rich aerosols are the dominating pollutants in marine environments and accelerate the corrosion rate drastically for many metals [18]. The aerosols are suspended in some small liquid or solid particles from salt spray and/or fog in the coastal environment [9]. The presence of chloride has detrimental effects on the stability of metal oxides or hydroxides, present on the surface of many metals, and that possess beneficial corrosion barrier properties. Deposition of these chloride-rich particles results in their dissolution in the aqueous layer on the metal surface and the interaction between dissolved chlorides and the surface oxide.

Corrosion effects at atmospheric conditions induced by the sulfate-rich particles have mainly been investigated for (NH₄)₂SO₄ deposition [1–3,19], a common constituent in aerosols in both urban and rural atmospheres. The presence of (NH₄)₂SO₄ has shown to result in even larger corrosion rates of Cu than NaCl-induced corrosion since NH₄⁺ evolves a series of reactions that catalyze the corrosion process [1]. Since the concentration of SO₄²⁻ in seawater is around 1/20 of the same for Cl⁻, this means that SO₄²⁻ is also present in sea-salt aerosols in marine environments [20]. Few or no studies exist that investigate the effect of Na₂SO₄ or the combined effect of Na₂SO₄ and NaCl on the atmospheric corrosion of Cu and Cu-based alloys at marine conditions.

2.3 Atmospheric corrosion of Cu

Copper is a metal of great importance in many applications such as in heat exchangers, microelectronics, and in construction. Patina, the corrosion product layer that gradually covers the surface of Cu or Cu-based alloys with time upon atmospheric exposure, is extremely stable after its establishment. It is protective for architectural and sculptural use and becomes a permanent part of the surface of the building or object. Cu and Cu-based alloys also play an important role in many situations, for example, for electrical purposes and cladding and façade applications on buildings, where the original surface characteristics should be maintained. For electrical applications, patina formation is not desirable as it reduces the conductivity [6].

There are many minerals and crystalline substances present on corroded copper surfaces, including oxides, hydroxides, sulfates, chlorides, carbonates and nitrates. At the very beginning of copper corrosion, cuprite (Cu₂O) is formed just in seconds. In sulfur-rich environments, amorphous copper sulfates form within days of exposure. Other crystalline products are formed over months and years, for example, brochantite [Cu₅SO₄(OH)₆], antlerite [Cu₃SO₄(OH)₄], and posnjakite [Cu₄SO₄(OH)₆H₂O], induced in sulfur-rich atmospheres, and atacamite [Cu₂Cl(OH)₃], in chloride-containing atmospheres. Brochantite is a major component in aged copper patinas exposed in rural, urban and industrial atmospheres, and also often the end-product of the patination process at these conditions. Antlerite is also a hydroxysulfate of copper formed in atmospheres of high pollutant levels of e.g. SO₂. It is a very common patina constituents reported in several studies on samples exposed for several decades. Posnjakite is another sulfate-rich corrosion product formed in patina, which is undergoing transformation to
brochantite with time due to its structural similarity. Atacamite, or its isomorphs, is the end corrosion product in chloride-rich atmospheres with nantokite (CuCl) as a precursor [6].

Lobnig et al. [2,3,19] demonstrated that the oxidation of copper is not affected by deposited (NH₄)₂SO₄ particles at a relative humidity below the “critical humidity”. At a relative humidity around the critical humidity point, 75% RH for (NH₄)₂SO₄, the formation of Cu₂O and basic copper sulfates were observed. At 88% RH, a continuous Cu₂O layer rapidly formed that was overgrown with time by antlerite crystals. Chen et al. [31] showed quantitative results of (NH₄)₂SO₄-induced atmospheric corrosion. Even at a low relative humidity of 70%, far below the deliquescence point at 81% RH, there was still significant corrosion on the surface and the corrosion products Cu₂O and antlerite were formed at the area of particle deposition. At 90% RH, the exposed samples formed a thicker Cu₂O layer, and small amount of copper sulfate and basic copper sulfate on top of the Cu₂O layer. The mass gain and mass loss of copper increased with exposure time. The study also showed (NH₄)₂SO₄ particles to be more corrosive than NaCl particles on copper, whereas opposite findings were observed on zinc [1].

In this study, the relative humidity introduced was 90% RH, that is much higher than the points of deliquescence of the pre-deposited salts, 81.7% RH for Na₂SO₄ [21], and 75% RH for NaCl at 25°C [12].

2.4 Atmospheric corrosion of Cu-based alloy (Cu5Al5Zn)

Cu5Al5Zn is a Cu-based alloy with golden color, denoted golden alloy, widely used in mintage and construction among European countries, for example, Swedish ten kronor coins and Eurozone’s 10 cent, 20 cent, and 50 cent coins [22]. Apart from its great mechanical properties, the low allergenic property is one reason why it is widely used in mintage. Most alloys used for mintage include nickel, which may induce dermatitis and allergic reactions to humans [33,24]. Cu-based alloys are also popular to use in outdoor constructions, for example, the facade of Sven-Harrys art museum in Stockholm, Sweden is made of Cu5Al5Zn. Thus, the corrosion resistance, especially at atmospheric corrosion, becomes more and more notable for this alloy. The alloy includes five weight percent of zinc (Zn), five weight percent of aluminum (Al), and one percent of tin (Sn). The corrosion behavior of the alloy requires knowledge on the influence of these alloy constituents on the evolution of corrosion products in the patina.

Atmospheric corrosion of zinc at natural weathering conditions has been widely investigated [25–27]. A scheme of the corrosion evolution of Zn has been established by Odnevall and Leygraf [8]. After seconds, zincite (ZnO) and zinc hydroxide [Zn(OH)₂] are rapidly formed on the surface and transformed into hydrozincite [Zn₅(OH)₆CO₃] within hours of exposure at humid conditions. This phase will evolve a transition from its amorphous to crystalline state with time. If chlorides are present in the atmosphere, zinc hydrochloride, simonkolleite [Zn₅(OH)₆Cl₂·H₂O], locally forms and eventually transforms to a sodium zinc hydroxychlorosulfate, gordaite, [NaZn₅Cl(OH)₆SO₄·6H₂O]. The presence of sulfur in the atmosphere results in the formation of different zinc hydroxysulfates, such as [Zn₅SO₄(OH)₆·nH₂O], and also zinc chlorohydroxysulfate [Zn₅Cl₂(OH)₆SO₄·5H₂O] in the presence of chloride.

Foster et al. [28] have studied the corrosion of Cu5Al5Zn and Cu in synthetic perspiration environment. Their findings show that the addition of Zn, Al, and Sn suppresses the corrosion layer formation during cyclic exposures compared with corresponding effects on Cu metal. The mass gain over 12 cycles exposure of Cu5Al5Zn was slightly lower than for Cu metal, which indicates less corrosion products formed on the Cu5Al5Zn surface than on the Cu metal. Odnevall et al. [4] investigated the atmospheric corrosion of Cu and three Cu-based alloys (including Cu5Al5Zn) in marine environments. The results
showed that the composition of the patina increased in complexity depending on the alloying constituents. Cu$_2$O in an inner layer and Cu$_2$(OH)$_3$Cl in an outer layer were observed for all materials. Additional patina constituents, for example, Zn/Al- hydroxycarbonates and chlorides, and Sn-oxides formed within the patina improving its barrier properties and reduced the chloride-induced corrosion process. This explains for instance why Cu$_5$Al$_5$Zn has an improved corrosion resistance compared with Cu metal at marine exposure conditions.
3. Experimental
The experimental approach conducted in this project is schematically illustrated in Figure 3.1, including sample preparation, salt deposition, laboratory exposure, and measurement techniques. Details are given below.

![Figure 3.1 Schematic illustration of the experimental approach.](image)

3.1 Materials, sample preparation and particle deposition
The metals used for exposure in this project include a commercial Cu alloy (Cu5Al5Zn) and Cu metal provided by International Copper Association, Belgium. The nominal bulk composition of Cu5Al5Zn, based on supplier information is shown in Table 3.1.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Cu</th>
<th>Al</th>
<th>Zn</th>
<th>Sn and others</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight percent (%)</td>
<td>89</td>
<td>5</td>
<td>5</td>
<td>1</td>
</tr>
</tbody>
</table>

The salts used for deposition include sodium sulfate, Na₂SO₄, provided by Merck Schuchardt OHG, Germany, and sodium chloride, NaCl, provided by Sigma-Aldrich, Germany.

The Cu5Al5Zn and Cu samples were cut to a dimension of 1×1 cm² for all laboratory exposures. The samples were abraded using silicon carbide paper up to 2400 grits, and then diamond polished from 3 to 1 µm. After polishing, the samples were ultrasonically cleaned in analytical grade ethanol for more than
15 min, followed by cold nitrogen blowing until the samples were completely dry. The polished samples were stored in the desiccator for 20 h before salt deposition and exposure in the climatic chamber.

![Figure 3.2 Suspension of salts with ethanol.](image)

Since Na$_2$SO$_4$ and NaCl are almost insoluble in ethanol, the salts were suspended in this solution to enable salt particles to be deposited on the surface in an as uniform way as possible. The salts were mixed with analytical grade ethanol and stored for 30 min until the mixture became stable. The upper volume of the suspension still contained a few suspended salt crystals for each salt, as illustrated in Figure 3.2. A defined volume of the suspension was then transferred with a pipette containing a given salt concentration onto the surface. Transferred volumes corresponded to the following mass of the salts; approx. 7 µL/cm$^2$ Na$_2$SO$_4$ equals a mass concentration of 10 µg/cm$^2$, and approx. 4 µL/cm$^2$ NaCl equals a concentration of 4 µg/cm$^2$ deposited on the sample surface, respectively. These masses (based on 20 unique measurements) were determined from the weighed mass of each salt left after ethanol evaporation. The weighing was performed using a Mettler Toledo Excellence microbalance with a precision of 2 µg.

### 3.2 Laboratory exposure

After surface preparation and salt deposition, the Cu and Cu5Al5Zn samples were placed into a WEISS WK1000 climatic chamber for repeated wet/dry cyclic exposures with humidity changes at room temperature (approx. 20 °C). The cyclic exposure program is shown in Figure 3.3. In the first cycle, the samples are exposed to a humid atmosphere of 90% RH for 4 h, followed by 2 h dry exposure. The second cycle starts after 16 h humid exposure with the same relative humidity and ends by a 2 h dry exposure. 6 and 14 cycles exposures repeat the first two cycles 3 and 7 times, corresponding to 3 and 7 days of exposure. All samples were exposed in parallel, and were investigated and analyzed by ex-situ techniques after these exposures [16].
3.3 Analytical techniques

Employed techniques and acquired information from each technique are compiled in Figure 3.4. The basic theory and the experimental parameters are given below.

![Schematic illustration of repeated wet/dry cycles during the laboratory exposure in a climatic chamber.](image)

Figure 3.3 Schematic illustration of repeated wet/dry cycles during the laboratory exposure in a climatic chamber. [16]

3.4 Light Optical Microscope (LOM)

Optical microscopy is a fundamental technique used to acquire magnified images when measuring samples by using a system of lenses and visible light, where the images can be captured by light-sensitive cameras [29].

The optical microscope used in this project is Leica DM 2700M microscope combined with high quality Leica optics with state-of-the-art universal white light LED illumination.

3.5 Scanning Electron Microscopy/Energy dispersive x-ray spectroscopy (SEM/EDS)

Scanning Electron Microscopy (SEM) is a technique to measure samples by means of striking the samples surface with a focused electron beam. The accelerated beam strikes the material with elastic and inelastic scattering, resulting in signals emission to be detected by a detector. The signal includes secondary electrons (SE), backscattered electrons (BSE), x-rays, and Auger electrons, which are used for imaging, qualitative and semi-quantitative investigations of materials. SE and BSE are normally used for
imaging where the x-ray signal is used to provide compositional information. Figure 3.5 shows the electron interaction volume on the sample surface \[30\].

![Figure 3.5 Interaction volumes for different electron-sample interactions. \[30\]](image)

High resolution images were generated using a FEG-SEM instrument, a LEO 1350 field emission gun SEM with a Gemini column, upgraded to a Zeiss Supra 55 column. The accelerated voltage used for the measurement was 15 kV using a 60 μm aperture size. EDS measurements were performed using a X-Max SDD detector (silicon drift detector) from Oxford Instrument \[16\].

### 3.6 Attenuated Total internal Reflectance Fourier Transform Infrared spectroscopy (ATR-FTIR)

Fourier Transform Infrared spectroscopy (FTIR) \[31\] is a technique to identify materials by analyzing the absorption or emission information from a surface. Attenuated Total internal Reflectance (ATR) is a method often combined with an FTIR instrument to obtain an improved resolution. ATR can also be used to analyze specific samples, such as powders, and aqueous liquids, which are difficult to measure by conventional FTIR \[32\].

![Figure 3.6 Theory of attenuated total internal reflectance. \[32\]](image)

The principle of ATR is based on total internal reflection. If a propagated wave strikes a boundary, where the two materials have different refractive index, shown in Figure 3.6 with \(n_1 > n_2\), and incident angle
larger than a so-called “critical angle”, the beam will not pass through and be reflected entirely. Total internal reflection occurs at this critical angle.

In fact, the beam is not reflected in total, as it penetrates the sample in some depth and comes back to the ATR crystal. The penetration depth is around 0.5 to 2 \( \mu \text{m} \), where the exact value depends on the incident angle, wavelength of light, indices of refraction for the ATR crystal and the medium being probed \([33]\). The sample will absorb some energy from the incident beam by its specific structure, and the detected difference between the incident beam and reflected beam will form a spectrum, a transmittance/absorbance spectrum, from which further structural and compositional information on the sample surface can be obtained.

The instrument used in this project was a Bruker LUMOS FTIR microscope.

3.7 Grazing incidence x-ray diffraction (GIXRD)

X-ray diffraction (XRD) is a technique to determine and provide information of crystalline phases of a material. According to Bragg's law, the incident x-ray diffracts a crystalline material to various angles \([34]\). The equation of Bragg's law is shown below, including wavelength of the beam (\(\lambda\)), the diffraction angle (\(\theta\)) and the lattice spacing (\(d\)) for a crystalline sample:

\[
n\lambda = 2d \sin \theta
\]

Grazing incidence x-ray diffraction (GIXRD) uses small incidence angles to increase the travel path, thereby increasing information from the outermost surface instead of providing mainly bulk information, which is typically collected by using traditional XRD. For the samples in this project, small amounts of corrosion products were present in a relatively thin surface layer. The more surface sensitive technique, GIXRD, was therefore used in this study.

GIXRD analyses were conducted by using a X’pert PRO PANALYTICAL system, equipped with an x-ray mirror (CuK\(\alpha\) or MoK\(\alpha\) radiation) and a 0.27° parallel plate collimator on the diffracted side. The scanned area was 1×1 cm\(^2\) at a grazing angle of 0.5° versus the surface \([16]\).

The reference PDF cards used in this study are, No. 00-005-0067 for Cu, No. 00-041-0254 for Cu\(_2\)O, and No. 00-004-0836 for CuO.

3.8 Cathodic reduction (CR)

Cathodic reduction is based on traditional electrochemical cell reactions to acquire information of corrosion products and estimate their amounts and relative thicknesses by applying a constant electric potential or current to reduce the oxides or other corrosion products. The set-up consists of four main components including a work electrode (WD), a reference electrode (RE), a counter electrode (CE), and an electrolyte. With the current is applied on the sample, the potential change over the time is recorded against a reference electrode. This technique is widely used to estimate the nature and thicknesses of corroded surfaces exposed at field and laboratory conditions \([35,36]\).

In the measurement, an oxide with a given thickness will result in a potential that is relatively constant over time at an applied current until it is fully reduced. This plateau is seen in the potential-time curve \([37]\). After full reduction, the potential drops until it reaches the reduction potential of another oxide or corrosion product. Each compound has a specific reduction potential that helps to identify components of the corroded surface.
After all oxides/constituents are reduced, the potential drops to a more negative value that corresponds to hydrogen evolution \((2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2(g))\). This indicates a complete reduction of oxidized components, and the potential will remain constant. Faraday’s law is used to calculate the thickness of the corroded surface: 

\[
d = \frac{10000 \times t \times I \times M}{A \times n \times \rho \times F}
\]

where \(d\) is the thickness of the reduced oxide (nm), \(t\) is the reduction time (s), \(I\) is the applied current (mA), \(M\) is the molar mass of the oxide layer (g/mole), \(A\) is the sample area in contact with the electrolyte (cm\(^2\)), \(n\) is the number of electrons required to reduce one mole of oxide, \(\rho\) is the density of the reduced oxide (g/cm\(^3\)), and \(F\) is the Faraday’s constant \((9.65 \times 10^4 \text{ C/mole})\).

A Solartron potentiostat/galvanostat model SI 1287 instrument was used for CR using a three-electrode system in which the Cu5Al5Zn alloy was used as working electrode, a platinum mesh as the counter electrode, and an Ag/AgCl reference electrode. All measurements were performed in a 0.1 M KCl electrolyte. The applied static current density was set to 0.05 mA/cm\(^2\). The KCl electrolyte was purged with N\(_2\) to remove the oxygen for 30 min before use \([16]\). The open circuit potential (OCP) was determined for all samples before the CR measurements.
4. Results and discussion

4.1 Particle deposition

For single salt deposition (10 µg/cm² or 16 µg/cm² Na₂SO₄ in this thesis), the distribution of salt crystals on the surface is shown in Figure 4.1. It shows that the Na₂SO₄ crystals, with the size of several microns, prefer to form clusters on the surface, instead of being homogeneously deposited over the surface.

Figure 4.1 10 µg/cm² Na₂SO₄ deposited on a Cu5Al5Zn surface at different magnification.

Figure 4.2 shows a SEM image of the area of pre-deposited Na₂SO₄ crystals and compositional information by EDS measurement. Compositional information is presented as the atomic fractions of Na, S, O, and bulk alloy elements (Cu, Al, Zn, Sn). The oxygen and sodium contents are mainly attributed to undissolved Na₂SO₄ crystals. The overlapping peaks between Na K-peak and Zn L-peak probably results in a higher content of Na than the real value. The theoretical atomic ratio between O and Na is 2:1. Significantly lower levels observed of S than expected (Na:S atomic ratio of 2:1) are most probably a result of low concentration levels and a large contribution from the bulk composition.

Figure 4.2 SEM/EDS results (atomic-%) of the area of pre-deposited Na₂SO₄ crystal.

Two methods were used to enable mixed salt deposition (4 µg/cm² NaCl + 10 µg/cm² Na₂SO₄). In the first method, NaCl was first deposited on the surface. After ethanol evaporation, Na₂SO₄ was deposited in the same way. Salt distribution images on the Cu5Al5Zn surface after NaCl deposition followed by Na₂SO₄ deposition are illustrated in Figure 4.3, which shows NaCl crystals preferably distributed homogeneously on the surface after ethanol evaporation, with a typical crystallite size of approximate 10 µm. The Na₂SO₄ particles were distributed in the same way as observed for single salt deposition, which resulted in their formation as clusters (sized >10 µm) in between the NaCl particles. Figure 4.4
shows compositional information obtained after deposition of the two salts on an area mainly covered by NaCl crystals. The oxygen content is much lower than Figure 4.2 showed due to limited amounts of Na$_2$SO$_4$ in this area.

![Figure 4.3 Mixed salt deposition on a Cu5Al5Zn surface (a) after NaCl deposition, and (b) after Na$_2$SO$_4$ addition.](image)

![Figure 4.4 SEM/EDS results (atomic-%) of a Cu5Al5Zn surface deposited with a mixture of NaCl and Na$_2$SO$_4$.](image)

In the second method the salts were mixed and deposited on the Cu5Al5Zn surface by using two transfer pipettes at the same time. The deposition pattern, after ethanol evaporation, is shown in Figure 4.5. The distribution of the two salt crystals was almost the same as observed with the first deposition method. After exposure, the results showed no large differences between the two deposition methods, either from a morphology or a corrosion evolution perspective, as illustrated in Appendix B. Thus, the mixed salt deposited samples were in the following deposited using the second method.

![Figure 4.5 Mixed salt deposited together on a Cu5Al5Zn surface at different magnification (LOM).](image)
4.2 Single Na$_2$SO$_4$ deposition on Cu and Cu5Al5Zn

4.2.1 LOM/SEM/EDS results

Figure 4.6 shows the evolution of pre-deposited areas on the Cu5Al5Zn surface under the same magnification. The corrosion cells evolved over time at areas of pre-deposited Na$_2$SO$_4$ salt clusters. Since the deposition of salts is not homogeneous, it is difficult to assess which sample is most corroded based on the small size of the measurements. An important aspect to consider is the secondary spreading area $^{[13,15]}$, where typically the cathodic reduction reactions take place and that easily could be observed after 14 cycles of exposure. These observations indicate further that atmospheric corrosion took place in areas of pre-deposited salts.

Figure 4.6 Surface changes under LOM of Cu5Al5Zn pre-deposited with 10 µg/cm$^2$ Na$_2$SO$_4$ and exposed to (a) 1 cycle (b) 2 cycles (c) 6 cycles and (d) 14 cycles of wet/dry conditions.

Figure 4.7 shows the morphology Cu5Al5Zn samples pre-deposited with 10 µg/cm$^2$ Na$_2$SO$_4$ exposed for 1, 2, 6, and 14 cycles analyzed by means of SEM and compositional information provided by EDS at these areas. The sodium and oxygen contents decreased dramatically after 1 cycle of exposure, which is attributed to the dissolution of Na$_2$SO$_4$ crystals due to the introduction of humidity. The amount of oxygen increased with exposure time within areas of pre-deposited salts. The reason is that EDS information is gained from a relatively large depth volume, from several micrometers to more than ten micrometers depending on the accelerating voltage for the instrument. The acceleration voltage was in this case 15 kV, which means that the information to a large extent originates from the salt crystals before being partially dissolved. After humidity introduction, the salt dissolves and forms corrosion products. From their limited thickness follows a large contribution of elemental information from the bulk rather than from corrosion products formed.

The oxygen content in the middle part (anode) of the corrosion cells increased drastically with increasing exposure time. This implies an increased formation rate of corrosion products, such as sulfur-containing
copper-rich corrosion products and copper oxides in anodic areas whereas less oxygen was observed in the peripheral area of the droplet. SO₄²⁻ moves to the anodic area of the droplet that is positive after electron loss, and forms corrosion products with Cu⁺⁺ and oxygen, while Na⁺ moves to the peripheral area of the droplet.

With increased exposure time, the pattern of corrosion cells became more evident, and secondary spreading areas could be observed after 14 cycles of exposure as illustrated in Figure 4.6 (d), showing a more corroded surface than observed after shorter exposure periods.
Figure 4.7 SEM/EDS results (atomic-%) of exposed Cu5Al5Zn surfaces pre-deposited with 10 µg/cm² Na₂SO₄ after (a) 1 cycle (b) 2 cycles (c) 6 cycles, and (d) 14 cycles at wet/dry conditions.

Figure 4.8 shows a faster corrosion process induced by a higher amount of deposited Na₂SO₄, compared with the corresponding evolution at a lower concentration of Na₂SO₄ (10 µg/cm²) in Figure 4.6, forming larger corrosion cells on the surface. Secondary spreading areas were observed already after 1 cycle compared with 14 cycles for the lower amount of deposited Na₂SO₄.

Figure 4.8 (d) shows furthermore several kinds of surface features of corroded areas. One is the typical corrosion cell pattern with an anodic part surrounded by a cathodic area, while the other pattern is similar to the cathodic part of a corrosion cell, which could be induced by the dissolution of tiny salt crystals after humidity introduction. Based on SEM/EDS measurements, the results show this latter pattern to be minor corroded as the composition was almost the same as observed for areas without any salt deposition.

Figure 4.8 Surface changes illustrated by means of LOM of the Cu5Al5Zn alloy pre-deposited with 16 µg/cm² Na₂SO₄ after exposures of (a) 1 cycle (b) 2 cycles (c) 6 cycles and (d) 14 cycles to wet/dry conditions.
Figure 4.9 shows compositional differences (SEM/EDS) between corroded areas of Cu5Al5Zn coupons pre-deposited with 10 µg/cm² or 16 µg/cm² Na₂SO₄ and exposed for 2 cycles. Larger sizes of the corrosion cells of the coupons pre-deposited with the higher Na₂SO₄ concentration compared with coupons exposed to the low amount of Na₂SO₄ indicate larger clusters of pre-deposited salts.

After the same exposure, the oxygen content within the corrosion area of the 16 µg/cm² Na₂SO₄ pre-deposited sample showed the same trend (though higher oxygen content) as observed for the surface pre-deposited with 10 µg/cm² Na₂SO₄, i.e. more oxygen in the middle of the corrosion cells (anodic areas). This implies a more rapid oxidation of the Cu5Al5Zn surface and the formation of more corrosion products.

Figure 4.9 SEM/EDS compositional analyses (atomic-%) of corroded areas of the Cu5Al5Zn alloy exposed for 2 cycles and pre-deposited with (a) 10 µg/cm² Na₂SO₄ and (b) 16 µg/cm² Na₂SO₄.

Figure 4.10 shows the 10 µg/cm² Na₂SO₄ pre-deposited area on Cu metal after 6 and 14 cycles of exposure. Similar kind of corrosion cells formed on the surface and the pattern was the same as observed for the Cu5Al5Zn samples. Secondary spreading areas of the corrosion cells were observed earlier (after 6 cycles) on the Cu metal surface compared with the Cu5Al5Zn surface (14 cycles), shown in Figure 4.6 (d). This indicates a more rapid corrosion process on the Cu metal surface than the Cu5Al5Zn surface at the same exposure conditions (same amount of salt deposition and exposure time).
Figure 4.10 Optical images by means of LOM of Cu metal pre-deposited with 10 µg/cm² Na₂SO₄ and exposed for (a) 6 and (b) 14 cycles of dry/wet laboratory conditions.

Figure 4.11 shows the SEM/EDS results for the Cu metal coupons shown in Figure 4.10. Similar to findings for the Cu5Al5Zn alloy, the results show an increased amount of oxygen with time within the pre-deposited area, especially in the center of the corrosion cells where anodic reactions occur.

Compared with findings for the Cu5Al5Zn samples under the same conditions as presented in Figure 4.7 (d), both materials showed a high amount of oxygen on the surface after 14 cycles of exposure, implying rapid corrosion in the presence of deposited salts.

4.2.2 ATR-FTIR results
ATR-FTIR measurements were performed to assign the type of corrosion products on the exposed surfaces. All spectra compared in Figure 4.12 are generated from the center (anodic area) of the
corrosion cells (blue spots, see in Appendix A). The spectra are presented after baseline corrections, where the spectra of peripheral parts (red curves) are used as baselines for each sample to clearly illustrate the difference between the middle and the peripheral parts of the corrosion cell. Since the spectra of peripheral areas almost have no change compared with the spectrum of unexposed sample, these spectra were used for background correction. The peaks at 1400 cm\(^{-1}\) and 1600 cm\(^{-1}\) do not reflect any corrosion products as they appear at the same positions even for unexposed samples, see in Appendix A.

According to the spectra in Figure 4.12, the SO\(_4^{2-}\) band at 1174 cm\(^{-1}\) showed the highest intensity for the pre-deposited area of the unexposed coupon, which corresponds to the undissolved Na\(_2\)SO\(_4\) crystals, whereas the band disappeared upon humidity introduction (1 cycle). The intensity of the sulfate peak at 1174 cm\(^{-1}\) increased with time (number of cycles). In addition, the intensity of the band assigned to hydroxyl groups around 3440 cm\(^{-1}\) increased to some extent with exposure time. This may imply the formation of corrosion products of different hydroxy sulfates in this area. Similar to observations made for Cu\(_2\)O (band at around 644 cm\(^{-1}\)[12,13,39]), its intensity increased with time implying a growth of Cu\(_2\)O with time, i.e. more corrosion with time. The band at around 640 cm\(^{-1}\) in the salt spectrum is due to SO\(_4^{2-}\) vibrations, and not related to Cu\(_2\)O [13,19].

![Figure 4.12 ATR-FTIR spectra of Cu5Al5Zn coupons pre-deposited with 10 µg/cm\(^2\) Na\(_2\)SO\(_4\) and exposed to 0 (salt), 1, 2, 6 and 14 dry/wet cycles.](image)

The spectra in Figure 4.13 are generated at the anodic areas of the corrosion cells of the Cu metal coupons after baseline correction, in the same way as made for the Cu5Al5Zn alloy presented above, i.e. using spectra from the peripheral areas of the corrosion cell as baselines for each sample. The spectra show the difference between the most corroded part (anode) and the peripheral part (treated as an unexposed surface), to enable comparison in the extent of corrosion between different exposure durations.

According to the spectra, the sulfate band (around 1170 cm\(^{-1}\)), the Cu\(_2\)O peak (around 644 cm\(^{-1}\)) and the hydroxyl group band (between 3300 cm\(^{-1}\) and 3500 cm\(^{-1}\)) were observed both after 6 and 14 cycles of exposure. More sulfate-containing corrosion products and Cu\(_2\)O were present on the surfaces after 14
cycles of dry/wet exposures compared with 6 cycles of exposure, *i.e.* the same trend as observed for exposed samples of Cu5Al5Zn.

*Figure 4.13 ATR-FTIR spectra of Cu metal pre-deposited with 10 µg/cm² Na₂SO₄ and exposed to 6 and 14 cycles of wet/dry conditions.*

Figure 4.14 shows the comparison between exposed Cu metal and Cu5Al5Zn samples exposed to the same conditions. The Cu5Al5Zn sample showed almost the same intensity of the sulfate band and the Cu₂O peak after 14 cycles of exposure, whereas more Cu₂O was formed on the Cu metal sample compared with the formation of sulfates. The ratio between Cu₂O and SO₄²⁻ peak intensities was approx. 3.5 after 14 cycles of exposure. The reason could be that the sulfate band may originate both from basic Cu sulfates and basic Zn sulfates for the Cu5Al5Zn alloy, since Zn also easily forms basic Zn sulfates in the presence of sulfur.⁴⁰ GIXRD measurements were carried out to further assign the corrosion products but no diffraction peaks were discerned. The reasons are that most corrosion products still are in their amorphous states and/or that the amount of corrosion products is limited.

*Figure 4.14 ATR-FTIR results of Cu metal and Cu5Al5Zn samples pre-deposited with 10 µg/cm² Na₂SO₄ and exposed for 14 cycles of dry/wet conditions.*
4.2.3 Summary - single Na$_2$SO$_4$ deposition on Cu metal and Cu5Al5Zn

The LOM, SEM/EDS and ATR-FTIR results show the topographical and compositional information of local corrosion cells formed on the Cu metal and the Cu5Al5Zn alloy surface. The secondary spreading area (cathodic area of the corrosion cell) formed earlier at higher concentrations of Na$_2$SO$_4$ and faster on the Cu metal than on Cu5Al5Zn under same conditions. The oxygen content within the corrosion area increased with increasing exposure time, and highest contents were observed in the center of pre-deposited areas (anodic area of the corrosion cell) for both the Cu metal and the Cu5Al5Zn samples. As for the Cu5Al5Zn samples, the intensities of the sulfate band and the Cu$_2$O peak were almost the same, whereas, the intensity of the Cu$_2$O peak was around 3.5 times higher than observed for the sulfate band on the Cu samples after 14 cycles of exposure. The reason could be the additional formation of basic zinc sulfates formed on the Cu5Al5Zn surface.

Schematic illustrations are presented in Figure 4.15 to elucidate the formation of corrosion products on Cu5Al5Zn and Cu metal samples pre-deposited with Na$_2$SO$_4$ and exposed to wet/dry conditions. As discussed above, the main corrosion products of Cu5Al5Zn sample were basic sulfates (could contain both Cu and Zn sulfates) and Cu$_2$O, while basic Cu sulfates and Cu$_2$O were the main corrosion products formed on Cu metal surface. The amount of corrosion products increased with time in both cases, though more slowly on the Cu5Al5Zn alloy compared with the Cu metal.

Figure 4.15 Schematic illustration of the formation of corrosion products on Cu5Al5Zn and Cu coupons pre-deposited with 10 µg/cm$^2$ Na$_2$SO$_4$ followed by wet/dry cyclic exposures.

4.3 Mixed salt deposition (NaCl + Na$_2$SO$_4$) on Cu5Al5Zn

Corrosion effects on the Cu5Al5Zn alloy using the same mole concentration of 10 µg/cm$^2$ Na$_2$SO$_4$ were compared with findings from Chang et al [41] using 4 µg/cm$^2$ NaCl. The Cu5Al5Zn samples pre-deposited with Na$_2$SO$_4$ were less corroded than surfaces deposited with NaCl, see section 4.4. The study hence continued to study corrosion induced by the deposition of mixed salts (4 µg/cm$^2$ NaCl + 10 µg/cm$^2$ Na$_2$SO$_4$) on Cu5Al5Zn samples to investigate possible synergistic effects. The mixed condition is furthermore more close to real-life conditions as discussed in section 2.2.

The mixed salt deposition distribution on Cu5Al5Zn surface is shown in Figure 4.5. The larger clusters are pre-deposited Na$_2$SO$_4$ crystals, where the other salt crystals are NaCl. It is important to note that the NaCl crystal size is much larger than Na$_2$SO$_4$, whereas the Na$_2$SO$_4$ crystals prefer to form clusters distributed over the surface. Due to these differences, different kinds of corrosion cells were formed on the surface, as determined by SEM/EDS and ATR-FTIR.
4.3.1 Corrosion on Cu5Al5Zn after 1 cycle wet/dry exposure

4.3.1.1 Na$_2$SO$_4$ +NaCl pre-deposited area (Mainly Na$_2$SO$_4$ induced corrosion)

According to Figure 3.16, the corrosion cell at the pre-deposited salt area consists mainly of Na$_2$SO$_4$ crystals according to the SEM/EDS and ATR-FTIR results. The sulfate peak appears in the center of this area combined with the most intense hydroxyl peak, which indicates the formation of basic sulfates. The Cu$_2$O peak intensity increased from the center of the corrosion cell to its peripheral areas. These findings are different from findings with Na$_2$SO$_4$ deposition only where the Cu$_2$O peak intensity was the highest in the center of the corrosion cell compared with peripheral areas, see in Appendix A. The reason is that Cu$_2$O was mainly formed in the center of the Na$_2$SO$_4$ induced corrosion cell, but in the case of the mixed salt cell, corrosion in the peripheral areas was also induced by NaCl after humidity introduction due to the dissolution of NaCl crystals. Since Cu$_2$O is the main corrosion product formed upon NaCl induced corrosion and Cl$^-$ ions are more corrosive than SO$_4^{2-}$, this results in a distribution of more Cu$_2$O in the peripheral areas of the corrosion cell compared with its center. Furthermore, sulfates formed on top of Cu$_2$O in the center of the corrosion cell, resulted in a reduced peak intensity of Cu$_2$O [19]. A band at approximately 1400 cm$^{-1}$ appeared in the spectrum of the middle area of the corrosion cell that may imply the formation of hydrozincite, Zn$_5$(CO$_3$)$_2$(OH)$_6$ [15,17].

The oxygen content was the highest in the middle of the corrosion cell, similar to findings on single Na$_2$SO$_4$ induced samples. However, when comparing the EDS results with Figure 4.7 (a), more oxygen was present on samples deposited with the mixed salt compared with samples with single Na$_2$SO$_4$ deposition. This indicates the formation of more corrosion products within the pre-deposited area for mixed salt deposited samples compared with samples deposited with Na$_2$SO$_4$ only.

![Figure 4.16 Results of Cu5Al5Zn pre-deposited with 10 µg/cm$^2$ Na$_2$SO$_4$ + 4 µg/cm$^2$ NaCl and exposed for 1 cycle of dry/wet conditions – a) ATR-FTIR image, b) ATR-FTIR spectra, c) SEM image, and d) EDS compositional analysis (atomic-%).]
4.3.1.2 \( \text{Na}_2\text{SO}_4 + \text{NaCl} \) pre-deposited area (Mainly \( \text{NaCl} \) induced corrosion)

Figure 4.17 shows analytical results from a \( \text{NaCl} \) pre-deposited area on Cu5Al5Zn as described in Figure 4.5. According to the ATR-FTIR result, \( \text{Cu}_2\text{O} \) was the main corrosion product within the pre-deposited area. All three measured spots imply high and almost similar intensities of the \( \text{Cu}_2\text{O} \) peak positioned around 644 cm\(^{-1}\). No large differences in peak positions were observed for the sulfate band (between 1100 cm\(^{-1}\) to 1200 cm\(^{-1}\)) between these spots. After exposure, there were still some undissolved \( \text{NaCl} \) crystals in the middle of this area as seen from the EDS result (due to large crystal size). The \( \text{CO}_3^{2-} \) and hydroxyl group bands at 1400 cm\(^{-1}\) and around 3300-3500 cm\(^{-1}\) may indicate the formation of hydrozincite, as illustrated in section 4.3.1.1.

According to Figure 4.16 and Figure 4.17, the EDS results showed that the largest oxygen content normally appeared in the middle of a corrosion cell and the peripheral parts contained less oxygen in the case of pre-deposition with \( \text{Na}_2\text{SO}_4 \). In the case of \( \text{NaCl} \) pre-deposition, the oxygen content remained almost the same for the entire corrosion cell. It seems that the \( \text{NaCl} \) crystals dissolve and spread to a larger area. The reason could be the difference in deliquescence points between the two salts, 81.7 RH% for \( \text{Na}_2\text{SO}_4 \) \(^{[21]} \), and 75 RH% for \( \text{NaCl} \) at 25°C \(^{[12]} \).

4.3.2 \( \text{NaCl} + \text{Na}_2\text{SO}_4 \) pre-deposited area after 2 and 6 wet/dry cycles

The typical \( \text{Na}_2\text{SO}_4 \) corrosion cell spectra (ATR-FTIR) shown after one cycle in Figure 4.16 were difficult to be observed on the corroded surface after 2 and 6 cycles. Even though the pattern looks like the \( \text{Na}_2\text{SO}_4 \) pre-deposited areas, \( \text{NaCl} \) had dissolved and spread further with time until it partially or fully covered
the Na$_2$SO$_4$ pre-deposited areas. Corrosion induced by NaCl could mainly be discerned for samples exposed for 2 and 6 cycles.

4.3.2.1 NaCl+ Na$_2$SO$_4$ pre-deposited area after 2 cycles of wet/dry exposure

According to the SEM/EDS result, there was still some undissolved NaCl in the middle of the pre-deposited salt particle area. The oxygen distribution within the measured area was similar (corrosion cells induced by NaCl) to the 1 cycle exposed sample shown in Figure 4.17, and almost the same amount of oxygen within the whole area. The oxygen content was higher after 2 cycles compared with 1 cycle.

The ATR-FTIR result showed more corrosion products in the middle of the salt pre-deposited area than at the peripheral areas, for instance, carbonates (around 1400 cm$^{-1}$) and hydroxides (3300 cm$^{-1}$ to 3500 cm$^{-1}$). Formed corrosion products may consist of Cu-rich and Zn-rich hydroxides and/or some carbonates [4,17]. The Cu$_2$O peak remained the same for all measured spots, indicating relatively large amounts of Cu$_2$O formed both at the center of the pre-deposited area (anode) and at its periphery where cathodic reactions take place. This is different from the samples deposited by Na$_2$SO$_4$ only that showed a large gradient between these areas after exposure. Since NaCl has a lower deliquescent point than Na$_2$SO$_4$, it results in corrosion that takes place also in the peripheral areas.

![Figure 4.18 Results of Cu5Al5Zn pre-deposited with 10 µg/cm$^2$ Na$_2$SO$_4$ + 4 µg/cm$^2$ NaCl and exposed for 2 cycles of dry/wet conditions – a) ATR-FTIR image, b) ATR-FTIR spectra, c) SEM image, and d) EDS compositional analysis (atomic-%).](image)

4.3.2.2 NaCl+ Na$_2$SO$_4$ pre-deposited area after 6 cycles of wet/dry exposure

Compared with the Cu5Al5Zn samples exposed for 2 cycles shown in Figure 4.18, the intensity of the hydroxyl group band in the salt pre-deposited area increased with time, Figure 4.19. The bands in the range of 800 cm$^{-1}$ to 1200 cm$^{-1}$ are probably due to Cu-O-H bending vibration mode. Both of them
indicate more hydroxides formed on the surface \[14\]. The intensity of the Cu$_2$O peak remained almost the same for the entire area, similar to observations made for conditions induced by NaCl only.

The oxygen content increased within the NaCl pre-deposited area with time, compared to findings in Figure 4.17 and Figure 4.18, i.e. increased corrosion with time.

![Image](image1.png)

Figure 4.19 Results of CuSAISZn pre-deposited with 10 µg/cm$^2$ Na$_2$SO$_4$ + 4 µg/cm$^2$ NaCl and exposed for 6 cycle of dry/wet conditions – a) ATR-FTIR image, b) ATR-FTIR spectra, c) SEM image, and d) EDS compositional analysis (atomic-%).

4.3.3 GIXRD results

GIXRD measurements were performed to investigate the possible presence of crystalline corrosion products on the exposed surfaces. The information depth was in the order of 50-200 nm. According to the spectra, Figure 3.20, Cu$_2$O was the main crystalline corrosion product present on all surfaces with the additional presence of CuO on samples exposed for 2 and 6 cycles \[42\]. No identification was possible of other corrosion products such as basic metal carbonates and/or basic metal sulfates suggested from the ATR-FTIR investigation. This implies their presence in their amorphous state or in too small quantities for detection. The intensity of the Cu$_2$O peaks around 37° (28) and 43° increased with time, which indicates an increased formation rate of Cu$_2$O with time.
4.3.4 Corrosion behavior for mixed salt deposition - summary

- For short exposures (1 cycle), two different kinds of corrosion cells were formed on the surface as a result of Na$_2$SO$_4$- and NaCl-induced corrosion. For the Na$_2$SO$_4$ induced corrosion cells, basic sulfates (copper and/or zinc) and Cu$_2$O formed in the center of the cells, similar to the findings for samples pre-deposited by Na$_2$SO$_4$ only. The main difference was the formation of more Cu$_2$O in the peripheral areas of the cells induced by NaCl dissolution and its spreading. For the NaCl induced corrosion cells, they were almost the same as the corrosion cells observed after longer time exposures (2 and 6 cycles).

- For longer exposures (> 2 cycles), no Na$_2$SO$_4$ induced corrosion cells were observed on the surface even though they looked similar. These corrosion cells were mainly induced by NaCl with Cu$_2$O that covered most of the corrosion cell and with the formation of some basic carbonates and hydroxysulfates within the cells. The amount of these additional corrosion products increased with time.

Schematic illustrations of differences in corrosion product formation are presented in Figure 4.21.
The amount of corrosion products increased with time, also shown next using cathodic reduction (section 4.4).

4.4 Cathodic reduction (CR) measurements on Cu5Al5Zn

Figure 4.22 shows cathodic reduction curves for Cu5Al5Zn pre-deposited with 10 µg/cm² Na₂SO₄, 4 µg/cm² NaCl, and 10 µg/cm² Na₂SO₄ + 4 µg/cm² NaCl after exposures to 1, 2 and 6 wet/dry cycles. CR was performed to estimate relative amounts (calculating an average thickness) of corrosion products. The applied static current was set to -0.05 mA/cm². The plateau from -0.55 V to -0.65 V in Figure 4.22 (a) is probably related to the reduction of basic sulfates, and the plateau from -0.9 V to -1.0 V, seen in all figures) is due to the reduction of crystalline Cu₂O. After the reduction of all corrosion products, the potential corresponds to the hydrogen evolution at around -1.15 V vs Ag/AgCl [43]. The reduction of CuO is not shown in this figure since its reduction potential is above -0.4 V.
The CR curves show an increased thickness (amount) of corrosion products with time for all samples. Estimated thicknesses of corrosion products formed on Cu5Al5Zn are compiled in Table 4.1, calculated by using Faraday’s law. To calculate an estimated thickness of sulfates formed on the Na2SO4 pre-deposited samples, the layer was simplified as brochantite \([\text{Cu}_4\text{SO}_4(\text{OH})_6]\), even though other basic sulfates such as posnjakite and zinc hydroxysulfate may be patina components. The other assumption is that only Cu2O is taken into account for the reduction from -0.9 V to -1.0 V, although other corrosion products including CuO and/or other carbonates and hydroxides exist on the surface. Further assumptions are that the corrosion products form homogeneously on the surface and that all products are reduced \([28,44–46]\). The CR results should hence only be used for relative comparisons.

The estimated patina thickness of Cu5Al5Zn pre-deposited with Na2SO4 only sums up the contribution from sulfate and cuprite, while the relative thickness for NaCl-induced corrosion and mixed salt-induced corrosion only comprise the estimated thickness of Cu2O. In order to assess possible synergistic effects, the total estimated thickness of a+b (single Na2SO4 + single NaCl) was calculated and compared with the thickness of the patina formed on Cu5Al5Zn pre-deposited with the mixed salts.

Table 4.1 Calculated relative average thickness (nm) of corrosion products formed on Cu5Al5Zn pre-deposited with different salt concentrations (single and mixed salts) and exposed to 1, 2 and 6 wet/dry cycles.

<table>
<thead>
<tr>
<th>Exposure time/Salt deposition</th>
<th>10 µg/cm² Na2SO4 (a)</th>
<th>4 µg/cm² NaCl (b)</th>
<th>a+b (Numerical)</th>
<th>10 µg/cm² Na2SO4 + 4 µg/cm² NaCl (c)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sulfates</td>
<td>Cuprite (Cu2O)</td>
<td>Total</td>
<td>Cuprite (Cu2O)</td>
</tr>
<tr>
<td>1 Cycle</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Products</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>12.9</td>
<td>15.6</td>
<td>28.5</td>
<td>77.2</td>
</tr>
<tr>
<td>2 Cycles</td>
<td>18.4</td>
<td>20.9</td>
<td>39.3</td>
<td>138.9</td>
</tr>
<tr>
<td>6 Cycles</td>
<td>24.0</td>
<td>28.4</td>
<td>52.4</td>
<td>172.9</td>
</tr>
</tbody>
</table>

The results show slightly increasing amounts (thicknesses) of basic sulfates and Cu2O formed on Cu5Al5Zn when pre-deposited to Na2SO4 only. The patina formed on Cu5Al5Zn pre-deposited with NaCl or mixed salts was much thicker. This indicates that Na2SO4 is not as corrosive as NaCl for Cu5Al5Zn. The results furthermore show Na2SO4 to be less corrosive than \((\text{NH}_4)_2\text{SO}_4\), a salt that according to a previous study by Chen et al.\([1]\), revealed to be more corrosive than NaCl on Cu metal. The reason may be explained by a reaction sequence catalyzed by NH3.

Limited synergistic effects were observed when comparing the estimated thicknesses of a+b (single Na2SO4 + single NaCl) with c (mixed salt) after 6 cycles exposure.
5. Conclusions

- Deposited Na$_2$SO$_4$ crystals preferred to form clusters on Cu5Al5Zn and Cu metal surface whereas deposited NaCl crystals were distributed homogeneously. The size of the Na$_2$SO$_4$ clusters increased with increasing deposition, resulting in more areas covered by the salt.

- Two methods were elaborated to enable mixed salt deposition, i) deposition of one salt followed by the other after ethanol evaporation, and ii) simultaneous deposition of the mixed salts. Both methods worked well and similarly.

- For single Na$_2$SO$_4$ pre-deposition on Cu5Al5Zn, the corrosion products were mainly Cu$_2$O and basic copper sulfates (Cu- and/or Zn) that formed in the center of corrosion cells. Their formation increased with time. The secondary spreading areas formed earlier with increased levels of pre-deposited salts, indicative of faster corrosion.

- For single Na$_2$SO$_4$ pre-deposition on Cu metal, the corrosion products were mainly Cu$_2$O and small amount of basic copper sulfates. The secondary spreading areas formed earlier on Cu metal than on Cu5Al5Zn, indicative of a faster corrosion rate on Cu metal. Na$_2$SO$_4$-induced corrosion was less significant compared with (NH$_4$)$_2$SO$_4$ on Cu metal.

- Pre-deposited mixed salt (Na$_2$SO$_4$ + NaCl) on Cu5Al5Zn revealed two different kinds of corrosion cells on the surface after short exposures (1 cycle), i.e. Na$_2$SO$_4$- and NaCl- induced corrosion cells. Basic sulfates and Cu$_2$O formed in the center of the Na$_2$SO$_4$ induced corrosion cells similar to the distribution of corrosion products on Cu5Al5Zn samples pre-deposited with Na$_2$SO$_4$ only. The main difference was the formation of more Cu$_2$O in the peripheral areas coupons pre-deposited with the mixed salt due to the dissolution and diffusion of NaCl crystals close to Na$_2$SO$_4$ clusters upon humidity introduction. Cu$_2$O was the main corrosion product in the case of NaCl induced corrosion cells.

- For longer exposed samples (2 and 6 cycles), only NaCl induced corrosion cells were observed on the Cu5Al5Zn surface, i.e. at the high relative humidity (90%), NaCl with lower deliquescence point than Na$_2$SO$_4$ dominates the corrosion process over the entire surface. The corrosion products consist mainly of Cu$_2$O that covers the entire corrosion cells with the formation of other carbonates and hydroxides in the periphery of the pre-deposited areas.

- Cathodic reduction was carried out to estimate the relative thickness of corrosion products on corroded Cu5Al5Zn coupons pre-deposited with the mixed salt in order to compare the corrosion effects of pre-deposition with mixed salts and single salts. Cu5Al5Zn pre-deposited with Na$_2$SO$_4$ only, showed similar calculated thicknesses (amount) of sulfate-rich corrosion products and Cu$_2$O after wet/dry cyclic exposure, while the patina induced by NaCl and by the mixed salt was much thicker. There seems a negative interplay between the mixed salt within a short time exposure (1 and 2 cycles) and a slight synergistic effect after 6 cycles of exposure.
6. Outlook

- Additional complementary techniques could be used to identify the nature of formed corrosion products, such as XPS and nano-IR.
- A higher concentration of pre-deposited Na\textsubscript{2}SO\textsubscript{4} is suggested to obtain a better understanding of Na\textsubscript{2}SO\textsubscript{4}-induced corrosion, instead of 10 µg/cm\textsuperscript{2}, since Na\textsubscript{2}SO\textsubscript{4} is not as corrosive as NaCl.
- Investigations of possible synergistic effects between two or several mixed salts on corrosion product formation could be investigated at *in-situ* conditions using spectroscopic techniques.
- Modified salt spray tests could be used to further mimic outdoor conditions.
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Appendix A - ATR-FTIR measured area for the samples in Figure 4.1 and Figure 4.6

Cu5Al5Zn after polishing.

Cu5Al5Zn after Na₂SO₄ deposition.

Cu5Al5Zn after 1 cycle exposure under 10 µg/cm² Na₂SO₄ deposition.
Cu5Al5Zn after 2 cycles exposure under 10 µg/cm² Na₂SO₄ deposition.

Cu5Al5Zn after 6 cycles exposure under 10 µg/cm² Na₂SO₄ deposition.

Cu5Al5Zn after 14 cycles exposure under 10 µg/cm² Na₂SO₄ deposition.
Appendix B - Optical pictures of mixed salt pre-deposited sample in section 4.1

Mixed salt deposited sample after 1 cycle exposure (first deposition method).

Mixed salt deposited sample after 1 cycle exposure (second deposition method).

Mixed salt deposited sample after 2 cycles exposure (second deposition method).
Mixed salt deposited sample after 6 cycles exposure (second deposition method).