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Development of accelerated corrosion tests involving alternative exposure to hostile gases, neutral salt spray and drying

Master of Science Thesis in the Master Degree Program Materials and Nanotechnology

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Abstract

In this thesis, a well proven corrosion testing method developed by *SP Technical
Research Institute of Sweden (SP)* ISO 21207 method B is modified in order to increase
even further the acceleration factor of corrosion attacks by 40%. The method combines
humidity cycling with conditioning, drying as well as exposure to corrosive substances
SO_2, NO_2 and NaCl solution.

ISO 21207 method B is modified into three modifications; Modification A, Modification
B and Modification C. In Modification A the concentration of gas is increased by 50% for
SO_2 and 25% for NO_2 during gas exposure. For Modification B the pH of the NaCl
solution is decreased to 3-4, during salt spray test. The last Modification C is a
combination between Modification A and B i.e. a higher concentration of gas and salt
spray at lower pH.

Coupons of aluminum, AluZn, carbon steel, copper and zinc are exposed, both at *SP* and
at *SAAB*. The geometrical size of the coupons are 25 cm^2 and the coupons are prepared by
grinding and polishing down to 9 µm diamond, washing with ethanol in ultrasonic bath,
drying in warm air and weighed before test. The coupons are then exposed to salt and
hostile gases according to ISO 21207 method B, Modification A, B and C. The corrosion
products are then removed by chemical pickling in ultrasonic bath and the total mass loss
is calculated. For evaluation of the corrosion products different analytical techniques are
used.

In this thesis copper is the most interesting metal since the method is mainly used for
electronic components where copper is the dominating metal.

In the case of copper all tests accelerate the corrosion rate but Modification C accelerates
the most. However, the corroded surface in Modification C is very different compared to
that of the coupons exposed to the standardized method ISO 21207 method B. Surface
analysis shows that the corrosion products are changed when exposing is done as in
Modification C.

Acknowledgement

In May 2011 I got in contact with Ingvar Eliasson, who works at *SP Technical Research Institute of Sweden*. He recommended me to speak to Adeline Flogård, Head of Group Surface Technology at *SP,* and that she might be able to offer me a master thesis project. The project Adeline had in mind regarded accelerating an existing corrosion testing method, and I decided to go for the project. Subsequently I got in contact with Professor Lars-Gunnar Johansson at Chalmers and he became my examiner for the master thesis that I was going to do at *SP*. I had some previous knowledge in the corrosion field from a course in my master program *Materials and nanotechnology*, and I was looking forward to the project at *SP*.

I came to *SP* at the end of August 2011 and started my research project. From the first day and during the upcoming five months at *SP* I have met many helpful coworkers. I would like to give a special thank you to my supervisor Adeline Flogård and to Ingvar Eliasson, Bo-Lennart Andersson, German Mara, Lena Lindman and Eskil Sahlin at *SP*. I would also like to thank my examiner Lars-Gunnar Johansson, Urban Jelvestam and Vratislav Langer at Chalmers.

At last I would like to thank my family and friends who have supported me during my master thesis project at *SP*.

Erika Callsen

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List of abbreviations

AluZn	Surface coating of steel that contains aluminum and zinc
Cl^-	Chloride ion
CrO_3	Chromium trioxide
EDX	Energy Dispersive X-ray
HCl	Hydrochloric acid
H^+	Hydrogen ion
H_3PO_4	Phosphoric acid
H_2NSO_4H	Amido sulphuric acid
IC	Ion Chromatography
ICP-MS	Inductively Coupled Plasma Mass Spectroscopy
ISO 21207	ISO standard method
MAAC	Methods for Acceleration of Ageing and Corrosion tests
NaCl	Sodium Chloride
NH_2CH_2COOH	Glycine
NO_2	Nitrogen dioxide
NO_3^-	Nitrate
SiC	Silicon carbide
SEM	Scanning Electron Microscopy
SO_2	Sulfur dioxide
SO_4^{2-}	Sulfate
XRD	X-ray Powder Diffraction
XPS	X-ray Photoelectron Spectroscopy

1 Introduction

Technical products and systems are becoming more and more complex. The demand for high reliability increases even though the time between idea for a product and production decreases. Accelerated corrosion testing methods are one way to predict the lifetime of a product. The development of better testing methods is continuously proceeding.

Accelerated corrosion tests are cyclic climate tests that assess metal surfaces ability to resist corrosion. Methods are developed for mimicking an actual corrosion process in nature.

In 1998 a method called *Accelerated Corrosion Test Involving Alternate Exposure for Hostile Gases, Neutral Salt Spray and Drying,* SP Method 2499, was developed. This accelerated corrosion testing method was developed after several tests outside in nature and in laboratory environment. The aim was to design an accelerated corrosion tests for electronic components. SP Method 2499 is today standardized at ISO level under the name ISO 21207. The test method was developed by *SP Technical Research Institute of Sweden (SP)* and the Swedish car and electronic industries to examine accelerated corrosion of electronic units. There are two variants of the method where test method A simulates a moderately aggressive traffic environment, while test method B simulates a more severe industrial or traffic environment. The most applicable test to the telecommunication sector is test *method B*.

In 2009 a European project was started, *Methods for Acceleration of Ageing and Corrosion tests* (MAAC). One part of that project (WP2) was to develop high accelerated corrosion test based on ISO 21207 method B. In WP 2 *SP*, *Ericsson AB* and *SAAB AB (SAAB)* were cooperating. The aim of MAAC WP2 was to modify the existing method in order to reduce the testing time by 40%. The test metals were aluminum, AluZn, carbon steel, copper and zinc but the most interesting metal was copper since it is present in electronic components.

This master thesis is a part of the MAAC project which shall be finished in 2012. And this thesis follows the same aim as the MAAC project. In order to reach the goal the testing time needs to be reduced to approximately three weeks, whereas the laboratory testing time for ISO 21207 method B is five weeks for products from the telecom industry. Three different modifications of ISO 21207 method B will be performed and the exposures will be tested on metal coupons of aluminum, AluZn, carbon steel, copper and zinc with the geometrical size of 25 cm^2.

This thesis focuses on corrosive effects of the hostile gaseous species SO_2 and NO_2 and also the effects of salt spray exposure in the presence of hydrochloric acid. One important factor is to see how the corrosion products change when modifying the ISO standard. The perfect outcome should be that the tests are accelerated without changing the corrosion products. The ISO standard test is designed especially for copper and therefor is corrosion products of corroded copper evaluated. Surface analysis is also done on corroded aluminum coupons to see if the corrosion products formed follow the same pattern as for copper coupons.

The surface analysis methods used in this master thesis are *Ion chromatography* (IC), *Inductively Coupled Plasma Mass Spectroscopy* (ICP-MS), *Scanning electron microscopy* (SEM), *X-ray photoelectron spectroscopy* (XPS) and *X-ray powder diffraction* (XRD).

2 Atmospheric corrosion

2.1 General definitions of corrosion and electrochemical reactions

Corrosion originates from the Latin word corrodere which means gnaw or to gnaw (E. Mattson, 2009). It is a phenomenon that results from a chemical reaction between a metal or metal alloy and its environment. In nature metals are present in chemical compounds such as minerals. Most of the corrosion reactions in nature atmosphere are electrochemical. An electrochemical reaction is characterized by electrons being absorbed or emitted, and can be summarized by the following reaction:

$$Ox + ne^- \xleftrightarrow{Ox \quad Red} Red \qquad\qquad (2.1)$$

Red is a reducing agent, *Ox* is an oxidant and *n* specifies the number of electrons present in the reaction (E. Mattson, 2009). An oxidation of a metal is called an anodic reaction and the reduction is called cathodic reaction. In an electrochemical reaction electrons moves between anode and cathode (Eriksson, 1992) (Jones, 1996).

The substrate for anodic and cathodic reactions is the metal and its oxide where electrons conduct whereas ions move in the electrolyte. The corrosion rate depends on the kinetics of the anodic and cathodic reaction, the conductivity of the electrolyte and also the electronic conductivity in the solid phases present. An anodic reaction on metal surface (M) is described in reaction (2.2) (Eriksson, 1992).

$$M \rightarrow M^{n+} + ne^- \qquad\qquad (2.2)$$

Due to oxygen in the atmosphere reaction (2.2) is usually balanced by oxygen reduction in reaction (2.3).

$$1/2O_2 + H_2O + 2e^- \rightarrow 2OH^- \qquad\qquad (2.3)$$

This reaction is a cathodic reaction (Eriksson, 1992).

For example the corrosion reactions on iron in presence of water are visualized in Figure 1. At the anode iron are oxidized and at the cathode oxygen is reduced. Rust is created due to reaction between iron ion and hydroxide ion.
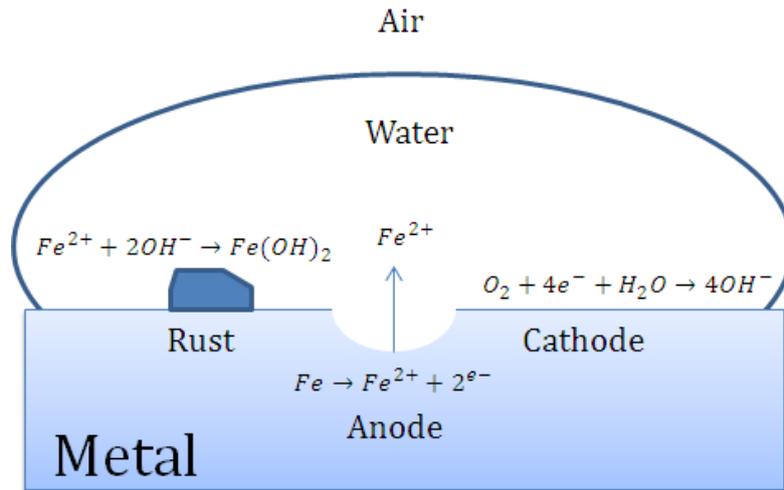
Figure 1 is an illustration of the corrosion process on a surface of iron. Iron forms ions at the anode and oxygen is reduced at the cathode. Reaction with aqueous iron and hydroxide creates rust.

2.2 Oxide layer formation

When a metal is exposed to air according to thermodynamics the metal is expected to form an oxide layer. Electrons in the oxidation process move toward the air-oxide interface and create an excess of negatively charged oxygen.

$$\tfrac{1}{2}\,O_2 + 2e^- \rightarrow O^{2-} \qquad\qquad (2.4)$$

At the metal-oxide interface a corresponding excess of positive ions is created. An important driving force for formation of oxide layer is potential difference between metal ion and adsorbed oxygen ion. A strong field increases the growth of an oxide layer due to greater driving force for metal ions through the oxide layer towards the oxide ions (Eriksson, 1992).

The oxide layer acts as a barrier to the anodic dissolution reaction. The state of when a protective oxide layer is formed is called passivity. However passivity does not occur without problems, the layer is thin and therefore fragile and can eventually atrophy and this can lead to corrosion attack (Jones, 1996). Pourbaix diagram of metals gives a graphically detailed description of how metals react at different pH and when the passive layer can be formed.

2.3 Influence of humidity and water

One requirement for atmospheric corrosion is humidity. A thin layer of water that deposits on the metal surface provides the electrolyte needed for electrochemical corrosion (Jones, 1996).

The term relative humidity (RH) describes the amount of moisture in air. The quantity of water molecule layers upon the metal depends on the RH and at about 25% RH the first layer starts to form. Formation of two layers water molecules starts at about 50% RH and the thickness of the layer increases sharply at 75% and 90% RH with 5 and 12 molecular layers (Eriksson, 1992).

In outdoor environment the metals will be exposed to a large amount of water on the surface as dew, fog and rain. The conductivity of pure water is poor but in outdoor environment the water always contains contaminants which can increase the low conductivity, being high enough to act as an electrolyte (Eriksson, 1992).

Pollutants can affect the aqueous surface film and can include the aqueous species H^+, SO_4^{2-}, NO_3^-, Cl^- and the gaseous species NO_2, SO_2 and also sea salt (Eriksson, 1992).

2.4 Acidic pollutants, inorganic gaseous pollutants and salts

The inorganic gaseous pollutants SO_2 and NO_2 tend to have corrosive effects on metals. In Sweden the industry stands for the majority of SO_2 pollutant while traffic stands for the majority of NO_2 pollutant. During year 2008 the SO_2 pollutant was measured to 31000 tons and NO_2 pollutant to 154000 tons (Naturvårdsverket, Utsläpp i siffror, 2010).

One reason why SO_2 accelerates the corrosion is high solubility. The dissolution of SO_2 in the water deposited on a metal surface follows (Eriksson, 1992):

$$SO_2(aq) + H_2O \rightarrow HSO_3^-(aq) + H^+(aq) \tag{2.5}$$
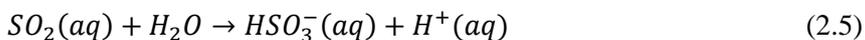
The oxidation reaction of SO_2 in water and air is described in (2.6).

$$SO_2(aq) + \frac{1}{2}O_2(aq) + H_2O(l) \rightarrow SO_4^{2-}(aq) + 2H^+(aq) \tag{2.6}$$
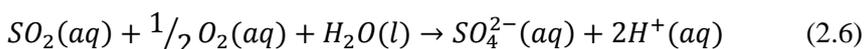
The existing oxide layer on the metal tends to dissolve when H^+ are present. By adding acid the rate of corrosion will speed up. The corrosion rate will increase even further if the water film deposit is dissolved and this is shown in reaction (2.7) (Eriksson, 1992).

$$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O \tag{2.7}$$

The hostile gaseous pollutant NO_2 originates via the oxidation of NO (g) and will be dissolved as described in reaction (2.8) (Eriksson, 1992).

$$2NO_2(g) + H_2O(l) \rightarrow 2H^+(aq) + NO_3^-(aq) + NO_2^-(aq) \qquad (2.8)$$
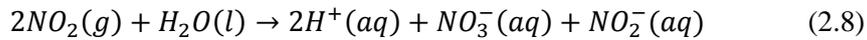
Deliquescent salts, such as NaCl, present lead to higher surface conductivity which increases corrosion. Increased ion transport is an explanation for the increasing corrosion rate (Jones, 1996).

2.5 The Pourbaix diagram and corrosion of copper

Pourbaix diagrams can describe more about how metals react in aqueous environment at different pH. This diagram is a function of polarization (E) and solution pH, in normal conditions of 25°C and 1 bar. In Figure 3 Pourbaix diagrams of aluminum, copper and zinc are shown. Every metal has an immunity region, a passivity region and a corrosion region in the Pourbaix diagram. When the metal has not oxidized it is immune and consists of only pure metal. In the passive region the metal has formed a protective oxide layer and the corrosion stops until the layer is broken down (Kurov, 2001).

The protective passive film can be dissolved due to a variety of effects, which are generally divided into physical and chemical effects. The physical effects can be volume changes or internal stress. Oxide breakdown of chemical effects can be introduced during ion adsorption at the surface or incorporation in the film. Generally formation of a stable protective film may be prevented by decreasing the pH (Zhang, 1996).
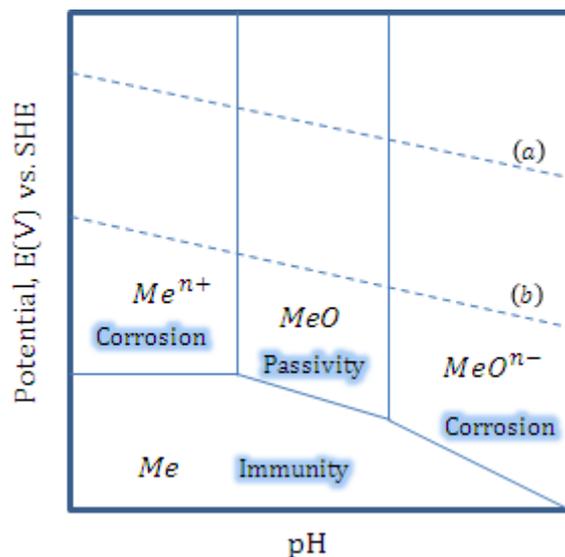
Figure 2 Illustration of a Pourbaix diagram of metal (Me) were n is the valence of ion. In the diagram there are corrosion regions, passivity region and immunity region. The dotted lines describe where water is stable.

Figure 2 is a schematic illustration of Pourbaix diagram of metal (Me). The dotted lines describe if oxygen, hydrogen or water is stable. Water is unstable above line (a) and will then oxidize to form O_2. Below line (a) water is stable and O_2 that is dissolved will be reduced to H_2O. Above the line (b) water is stable and if H_2 is present it will oxidize to H^+ or H_2O. In the region of immunity the metal consists of only pure metal and is thermodynamically immune to corrosion. The surface top layer of the metal in the passivity region consists of a thin solid oxide film that protects the surface from corrosion. In the left region of corrosion the metal has oxidized and at the right the passive oxide layer has dissolved leading to formation of metal oxide ion (University, 2007).
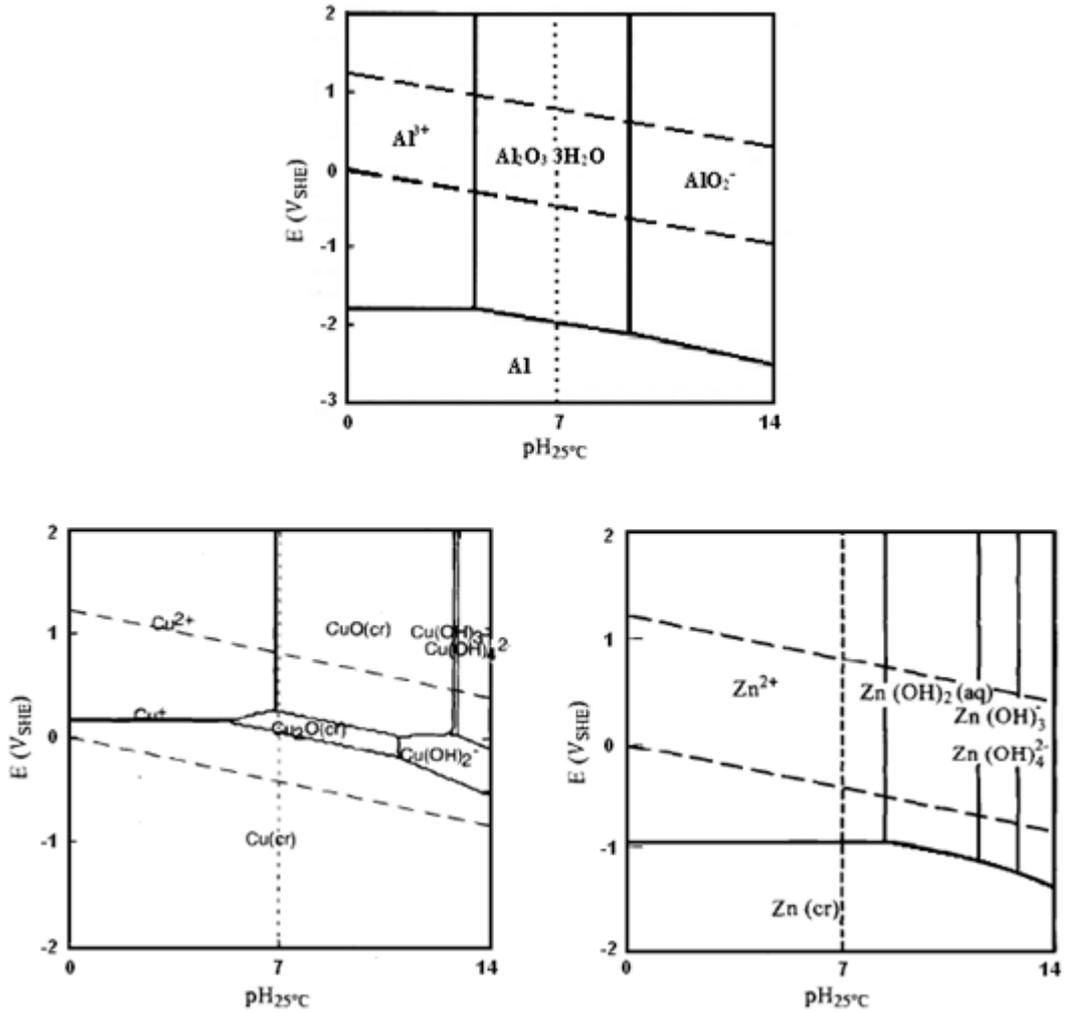
Figure 3 Pourbaix diagram of aluminum on the top, copper down at left and zinc down at right (B. Beverskog, 1997)

This thesis focuses on how the copper metal reacts when exposed to corrosion tests. One part of tests contains exposure in acidic environment. In the Pourbaix diagram for copper Figure 3 corrosion will occur when copper ions or copper oxide ions are formed, for example Cu^{2+} and CuO_2^{2-}. Protective oxide layers are created in the regions of CuO and Cu_2O were the oxide is solid and stable. In these regions there is a driving force to corrosion but the solid oxide creates a thin film and protects the surface. In the region of pure Cu the metal is thermodynamically stable and immune (E. Mattson, 2009).

The corrosion products formed on copper surface during exposure to neutral salts, such as NaCl, and to hostile gaseous species SO_2 are described in this section. The oxidation of copper is described in reaction (2.9). Copper ions can react with oxygen ions from

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reaction (2.4) and form an oxide layer of Cu_2O. This oxide layer has a mixed color of black and red.

$$Cu(II) \rightarrow Cu^{2+} + 2e^- \tag{2.9}$$

When copper is exposed to neutral salt a layer of $Cu_2Cl(OH)_3$ can be build up during reaction with OH⁻ and Cl⁻, as in reaction (2.11), and this compound is green. The formation of OH⁻ ions are shown in reaction (2.10).

$$^1/_2\, O_2 + 4e^- + H_2O \rightarrow 4OH^- \tag{2.10}$$

$$2Cu^{2+}(aq) + 3OH^- + Cl^- \rightarrow Cu_2Cl(OH)_3 \tag{2.11}$$
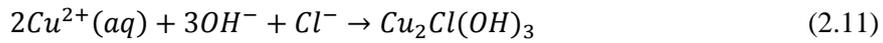
When copper is exposed to the hostile gaseous species SO_2 a layer of $CuSO_4(H_2O)_5$ can be created and is recognized by blue color. The oxide layer $CuSO_4(H_2O)_5$ is produced from reaction between SO_4^{2-} ion, Cu^{2+} ion and H_2O. One other possibility is reaction between SO_4^{2-} ion, Cu^{2+} ion and OH⁻ ion and this reaction will produce an oxide layer of $Cu_4(OH)_2SO_4 \cdot XH_2O$.

3 Analytical methods

To evaluate corrosion products several analytical techniques can be used. For a more complete outcome one single technique is seldom used. The most common techniques used for analyzing corrosion products can be divided into three groups; imaging techniques, elemental analyzing techniques and phase detection techniques (Pettersson, 2008).

This thesis focuses on evaluating the corrosion products with the analytical methods IC, ICP-MS, EDX and XPS for elemental composition, SEM for morphology studies and XRD for phase detection.

3.1 IC and ICP-MS

IC is a technique that can be used for determination of ionic species and their concentration. The chromatography technique is widely used for separating mixtures and provides both quantitative and qualitative information. The principle behind chromatography is to separate components by having two phases, one that is held in place (stationary phase) and one that moves (mobile phase). The separation is done in a column with packing as stationary phase and the mobile phase suspended in the solvent. For IC the stationary phase is provided by charged functional groups which perform the separation (Harris, 2002) (Skogsindustrierna, 2011). Conductivity detectors are common as IC detectors and do respond to all ions.

Another analytical technique for elemental composition is ICP-MS, where the ICP converts elements to ions and they are detected by MS (Ruth E. Wolf, 2005). The principle in ICP-MS is to generate positive ions by the use of high temperature plasma discharge. When the sample is pumped in the plasma the sample will travel through different heating zones which lead to vaporization and ionization. In the analytical zone of plasma there is enough energy to generate an ion. These ions are then detected by MS (Thomas, 2001).

3.2 SEM

SEM is a surface analysis technique for morphology studies of samples and the technique also offers information about which elements the surface consists of by detection of EDX. From the source of an electron gun a high energy electron beam is obtained. The electron beam scans over the sample and incident electrons are causing secondary electrons to be generated. The emitted secondary electrons are detected and gathered onto a phosphor screen. One important qualification of the sample is that it needs to be conducting and withstand vacuum. The EDX detector detects X-rays generated from the incident electrons; this is a commonly used detector in SEM. Mapping gives the lateral distribution of individual elements on the analyzed surface. The distribution of each element is shown in a separate image. A brighter color in the image means a higher occurrence of the element. The samples are not destroyed during the run with SEM-EDX which is a great advantage (Pettersson, 2008) (J.D. O'Connor, 1992).

Quantitative results from SEM-EDX are possible but one requirement is a smooth surface. For pure metal after grinding and polishing quantitative analysis is possible. But for corroded metals the corrosion products can be lost and destroyed during polishing. One possibility is to examine a polished cross section of the non-smooth sample.

3.3 X-ray Photoelectron Spectroscopy

Albert Einstein is the outliner of the phenomenon photoelectric effect and the surface analysis technique XPS is based on that phenomenon. The technique is very surface-sensitive and provides information on both elemental composition and oxidation states. A schematic image of the phenomenon photoelectric effect is pictured in Figure 4.
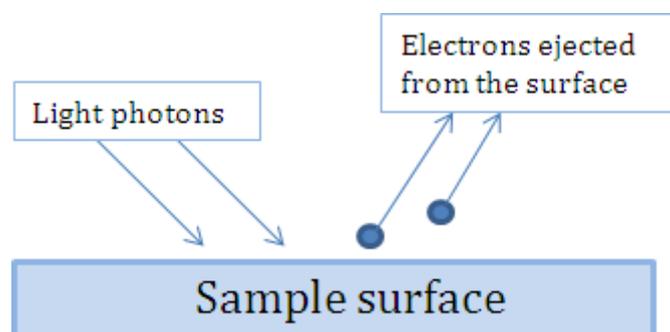

Figure 4 Illustration of the photoelectric effect where electrons are ejected from the surface.

The technique offers information about the chemical bonding and due to short range of the excited photoelectrons the sensitivity offers specific information. XPS can also offer

information about the chemical bonding. The technique also goes under the name Electron Spectroscopy for Chemical Analysis (ESCA) (J.D. O'Connor, 1992).

3.4 X-ray powder diffraction

The surface analyzis technique XRD gives information about crystallographic structure, chemical composition and physical properties of materials. The technique can also be used for identification of crystalline phases in corrosion products. XRD is widely used when it comes to identification of minerals and inorganic compounds.

In this technique X-rays are generated from a cathode ray and the ray is filtered for production of monochromic radiation. To concentrate the ray the line of sight needs to be adjusted before it is directed towards the sample. By interaction between the incident rays and the sample a constructive interference is produced and the conditions need to satisfy Bragg's Law (Collage, 2011).

$$n\lambda = 2d \sin \theta \qquad\qquad (3.1)$$

Where λ is the wavelength of incoming beam, n is the refractive index of the material, θ is the angle of incidence and d is the periodicity.

4 ISO 21207

ISO 21207 is an accelerated corrosion test which aim is to mimic the corrosion outside in nature for electronic components. Accelerated corrosion tests are very important for many companies and industries that produce technical products, especially products that will be held outside.

SP developed SP method 2499 and it became standardized at ISO level with the name ISO 21207. It is an accelerated corrosion test for simulating the effects of the most important factors enhancing the corrosion of metallic materials in an industrial and traffic environment. This testing method was developed to predict service lifetime especially for electronics and simulate a lifetime in tough road environment. Copper is the dominating metal in electronics and the standardized method is therefore made especially for material containing copper. In ISO 21207 there are two methods A and B and this thesis will focus on method B which is more applicable to the telecommunication sector.

4.1 ISO 21207 method B

The corrosion testing ISO 21207 method B involves alternative exposure to hostile gases, neutral salt spray and drying according to the following test cycle (Eriksson & Carlsson, 1998):

The test cycle starts with exposure to neutral salt spray containing 5 % NaCl in a salt spray cabinet at 35°C for 2 hours according to the standard *SS-ISO 9227*. After salt exposure the test objects are dried for 22 hours in constant climate room at 23°C and 50% RH.

After drying the test objects are exposed to 10 ppm NO_2 and 5 ppm SO_2 for 48 hours in a climatic cabinet with the conditions of 25°C and 95% RH. This is followed by exposure to neutral salt spray for 2 hours at the same conditions as in the start of the cycle according to *SS-ISO 9227* and then drying for 22 hours in constant climate room.

The 1-week cycle ends with exposure in climate cabinet at 10 ppm NO_2 and 5 ppm SO_2 at 25°C and 95% RH for 72 hours.

Table 1 One week of test cycle with ISO 21207 method B.

One week of ISO 21207 method B				
Monday	**Tuesday**	**Wednesday**	**Thursday**	**Friday**
Salt spray 2h Drying 22 h	Gas exposure 48 h		Salt spray 2h Drying 22 h	Gas exposure 72 h

One cycle of this test corresponds to one week of exposure. Table 1 describes the test cycle from a weekly perspective and the recommended periods of exposure are described in Table 2.

Table 2 The recommended test duration corresponding to years of exposure in the environment.

Test method	Type of environment	Years in environment	Test duration
ISO 21207 Method B	Industrial	3 8 14	1 week 2 weeks 3 weeks

5 MAAC

Methods for Acceleration of Ageing and Corrosion tests also called MAAC is a European project that started 2009 and contains development of high accelerated corrosion test based on ISO 21207 method B for the telecom industry. The aim of that project is to modify the existing test method in order to reduce the test time by 40%. In order to achieve the aim the testing time needs to be reduced to approximately three weeks, whereas the laboratory testing time for ISO 21207 method B is five weeks for products from the telecom industry. Three different modifications of ISO 21207 method B are tested and the exposures are performed on metal coupons. The following modifications are designed:

Modification A is an increase of the concentration of gas by 50% for SO_2 and by 25% for NO_2. The other parameters are unchanged compared to the original method.

Modification B is a decrease of pH to 3-4 during the salt spray exposure. The other parameters are unchanged compared to the original method.

Modification C is an increase of the concentration of gas as in Modification A as well as decrease of pH during salt spray exposure as in Modification B.

6 Experiments

This thesis focused on the development of ISO 21207 method B by accelerating the corrosion with three different modifications on metals. This section clarifies the material and methods used.

6.1 Materials

The materials used are summarized in Table 3:

Table 3 Chemical composition of the material used for the accelerated corrosion testing methods.

Metal	Composition %
Aluminum	≥ 99.5
AluZn	Al 55, Si 1.6, Zn 43.4
Cold rolled carbon steel	C 0.08, Mn 0.45, P 0.03, S 0.03, Fe 98.41
Copper	≥ 99.85
Zinc	≥ 99

6.2 Sample polishing preparation prior to testing

The metal coupons are first cut to the geometrical size of 25 cm^2 and then the metal surface are grinded and polished on both sides with Struers Tegra system. Silicon carbide (SiC) papers and water are used for grinding, and for polishing PAN disc and diamond solution are used. The grain size of SiC to start with depends on the metals. Table 4 describes how the coupons are grinded and polished.

Table 4 Polishing and grinding preparation before testing for the metal coupons used.

Metal coupons	Polishing preparation procedure
Aluminum	No polishing preparation
AluZn	No polishing preparation
Carbon steel	Mechanical grinded on SiC paper with grit 80, 220 and 500 in water and with 9 µm diamond spray manually
Copper	Mechanical grinded with SiC paper with grit 220 in water and polished with diamond 15µm
Zinc	Grinded manually with SiC paper with grit 1000 and 4000 on both sides

All coupons are marked with numbers and decreased in ethanol using ultrasonic bath. After cleaning the panels are dried in warm air and left in a desiccator in a constant climate room of 23°C and 50 % RH. The reference panels are weighted before test.

6.3 Accelerated corrosion testing

Accelerated corrosion testing is performed as in ISO 21207 method B and with Modification A, B and C. Two sets of each modification are performed at *SP* and *SAAB*. The coupons from *SP* and *SAAB* are compared to see if there are any differences. One complete test is three weeks and one week is as explained in Table 1.

6.3.1 Salt exposure

Each test cycle starts with salt spray exposure. For Modification A the metal coupons are placed in the salt spray cabinet and are exposed for 5 % sodium chloride salt solution with pH 6.5 to 7.2 at 35 °C according to ISO 9227. After one hour of testing the panels orientation is changed so that both sides of the coupons are exposed to the salt spray. The coupons are removed from the salt cabinet after 2 hours of testing and stored in a constant climate room at 23 ± 2°C and 50 ± 5% RH.

For Modification B and C the pH in the salt spray solution is changed from neutral to 3.5 by adding HCl.

6.3.2 Gas exposure

After salt spray exposure and storage the metal coupons are exposed to inorganic air pollutants. The conditions of 25 ± 1 °C and 95 ± 2 % RH are adjusted in the climate cabinet for air pollutant exposure test. For Modification A and C the amounts of air pollutants are adjusted to 12.5 ppm of SO_2 and 7.5 ppm NO_2. And for Modification B the amounts are adjusted to 10 ppm SO_2 and 5 ppm NO_2. The coupons are exposed to the inorganic gases in the climate cabinet for 48 hours respectively 72 hours during one cycle.

6.4 Mass loss calculation

The total mass gain of the coupons is measured after test and the mass loss is determined after repetitive chemical pickling according to ISO 8407. Coupons exposed at *SP* and *SAAB* are pickled at *SP*. The coupons are immersed into the chemical agent for pickling in ultrasonic bath for specific time depending on the metal.

The chemical pickling solution for aluminum contains 50 ml H_3PO_4 and 20 g CrO_3 per liter deionized water. The aluminum coupons are immersed into the chemical agent at 60 °C in ultrasonic bath for 5 minutes and then rinsed twice in warm water.

AluZn and zinc are pickled in a solution that contains 250 g NH_2CH_2COOH per liter deionized water. The pickling time for AluZn and zinc coupons is 5 minutes in ultrasonic bath and then rinsed once in warm water.

Carbon steel coupons are pickled repetitively in HCl in water (1:1) with hexamethylentetramine as an inhibitor for 10 minutes in ultrasonic bath and then rinsed once in warm water. After every pickling step the surface of the coupons is scratched with a wooden stick to remove more of the corrosion products.

Copper coupons are repetitively pickled in H_2NSO_4H (5% in weight) for 15 minutes in ultrasonic bath and rinsed twice in warm water.

After each pickling step all coupons are rinsed in ethanol and dried in warm air. For temperature equalization the coupons are stored for 30 minutes in a desiccator and then weighted. The pickling procedure is repeated for all coupons until all corrosion products are removed and a constant mass loss is measured.

6.5 Surface analysis

Methods used for surface analysis of copper and aluminum are IC, ICP-MS, SEM-EDX, XPS and XRD. The coupons are divided into four pieces each with an area of approximately 6 cm^2. For XPS and XRD no further sample preparation is needed.

With SEM-EDX the cross section of the copper and aluminum coupons are analyzed. in order to examining the cross section, the coupons of 6 cm^2 are molded into epoxy and then polished down mechanically to 1 μm with diamond spray to create a smooth surface. As the corrosion products are not conductive and in order to be examined with SEM, the samples are then coated with an ultrathin layer of carbon.

For ion chromatography the corrosion products are removed with a scalpel. Water soluble chlorides Cl$^-$ and sulfates SO$_4^{2-}$ were determined with ion chromatography and a conductivity detector, after the samples are dissolved in water. Water soluble sulfur was calculated from the amount of water soluble sulfate and the total amount of chloride is determined with ICP-MS.

7 Results

In this section results of mass loss from aluminum, AluZn, carbon steel, copper and zinc coupons are presented in tables. Each type of metal has been tested for Modification A, B and C at *SP* and *SAAB*. The mass loss results for coupons from *SP* and *SAAB* have been separated in the tables.

Results from surface analysis of aluminum and copper coupons with IC, ICP-MS, SEM, XPS and XRD are also presented in this section. The analyzed aluminum coupons have been tested with the standardized test method ISO 21207 method B and with Modification C at *SP*. The analyzed copper coupons have been tested with standardized method ISO 21207 method B and Modification B and C at *SP*.

In every mass loss table there is a mass loss value of the metal coupon tested with ISO 21207 method B at *SP*. This value is compared with the mass loss from the different modifications.

7.1 Mass loss of aluminum

In Figure 5 three images of aluminum are presented one before test, one after test Modification B and one after test Modification C. As can be seen on the pictures there is a great difference between before and after test. The layer of aluminum oxides after test is thick and very porous. One difference between the result from Modification B and C is that the surface of the aluminum coupons after Modification C shows dark spots.

Figure 5 Pictures of before and after test ISO 21207 method B, Modification B (Mod B) and Modification C (Mod C) of aluminum coupons.

The total mass loss for each individual test for aluminum coupons is presented in Table 5. From this table the mass loss increase or decrease in percent compared to the original method ISO 21207 method B is calculated and presented in Figure 6.

Table 5 Mass loss results for SP aluminum coupons and SAAB aluminum coupons from testing methods ISO 21207 method B and Modification A, B and C (Mod A, B and C). Two tests on each modification.

Mass loss of Al mg/dm² SP coupons								
	ISO 21207 B		Mod A		Mod B		Mod C	
Test 1 and 2	100	-	332	195	213	153	249	507
Mass loss of Al mg/dm² SAAB coupons								
	ISO 21207 B		Mod A		Mod B		Mod C	
Test 1 and 2	-	-	160	137	80	80	90	-

In Table 5 the mass loss from *SP* is greater than for *SAAB*. The mass loss values have increased compared to the standard method in every modification for *SP* but for *SAAB* only for Modification A. In Figure 6 it can be seen that the corrosion rate has increased for every modification except for Modification B for *SAAB*.
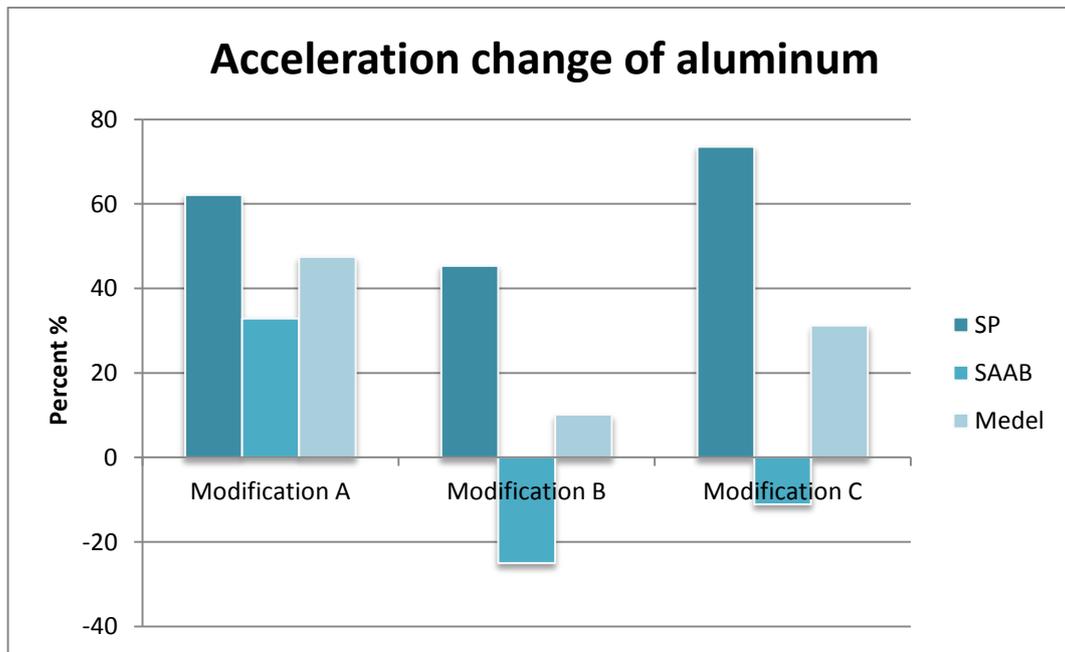
Figure 6 This bar chart describes the acceleration change in percent for all modifications for corroded aluminum coupons compared to the standardized method.

7.2 Mass loss of AluZn

In Figure 7 pictures of AluZinc before and after test ISO 21207 method B Modification C are presented. The oxide layer after corrosion test is thin and not porous.
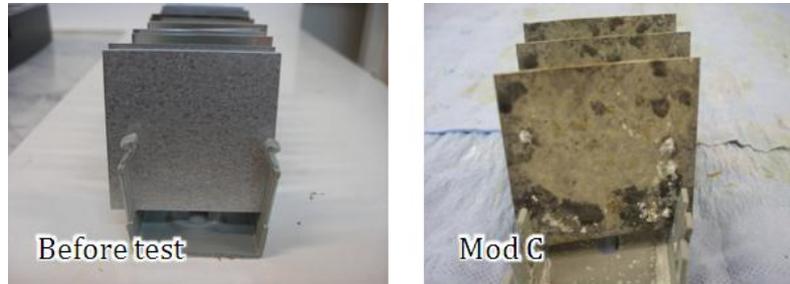

Figure 7 Pictures before and after test ISO 21207 method B Modification C (Mod C) of AluZn coupons.

For AluZn there is no reference mass loss value from ISO 21207 method B tested at *SP*. A table of mass loss results from AluZn coupons is presented in Table 6.

Table 6 Mass loss results for SP AluZn coupons and SAAB AluZn coupons from testing methods ISO 21207 method B and Modification A, B and C(Mod A, B and C). Two tests on each modification.

Mass loss of AluZn mg/dm^2 SP coupons							
	ISO 21207 B		Mod A		Mod B		Mod C
Test 1 and 2	-	-	359	560	320	-	265	-

Mass loss of AluZn mg/dm^2 SAAB coupons							
	ISO 21207 B		Mod A		Mod B		Mod C
Test 1 and 2	-	-	58	51	140	40	29	-

The mass loss results for AluZn show significant differences depending on being tested at *SP* or *SAAB*. Due to no reference value for AluZn from testing method ISO 21207 method B a percentage diagram cannot be made.

7.3 Mass loss of carbon steel

In Figure 8 coupons of carbon steel before test, after test Modification B and after test Modification C can be seen. The oxide layer is very thick after test. One difference between *SP* and *SAAB* coupons is that the thick layer of oxides falls of easily for *SAAB* coupons.

Figure 8 Pictures before and after test ISO 21207 method B Modification B (Mod B) and Modification C (Mod C) of carbon steel coupons.

From the mass loss reported in Table 7 a significant difference in mass loss can be seen for *SP* and *SAAB*.

Table 7 Mass loss results for SP carbon steel coupons and SAAB carbon steel coupons from testing methods ISO 21207 method B and Modification A, B and C (Mod A, B and C). Two tests on each modification.

| Mass loss of Carbon steel mg/dm² SP coupons							
	ISO 21207 B		Mod A		Mod B		Mod C	
Test 1 and 2	2600	-	7000	3222	5365	6518	5480	4455
Mass loss of Carbon steel mg/dm² SAAB coupons							
	ISO 21207 B		Mod A		Mod B		Mod C	
Test 1 and 2	-	-	1744	1984	2790	3711	4113	-
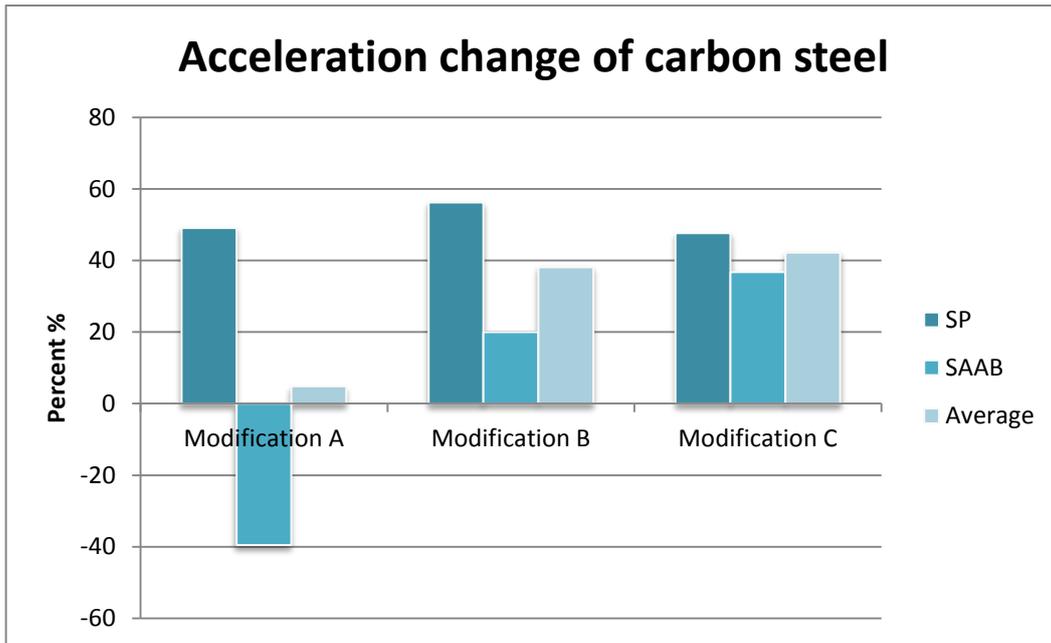
Figure 9 This bar chart describes the acceleration change in percent for all modifications for corroded carbon steel coupons compared to the standardized method.

7.4 Mass loss of copper

In Figure 10 copper coupons before test and after test Modification B and Modification C are presented. After corrosion testing with Modification B a thin layer of oxide has been formed. Green spots can be seen at the copper surface. After test with Modification C the green spots are more bluish and the spots are crystal like.

Figure 10 Pictures of copper coupons before and after test ISO 21207 method B Modification B (Mod B) and Modification C (Mod C).

In Table 8 the mass loss results from copper can be seen. Even in this case there is a difference between *SP* and *SAAB* coupons.

Table 8 Mass loss results for SP copper coupons and SAAB copper coupons from testing methods ISO 21207 method B and Modification A, B and C (Mod A, B and C). Two tests on each modification.

Mass loss of Cu mg/dm² SP coupons							
	ISO 21207 B		Mod A		Mod B		Mod C	
Test 1 and 2	400	-	682	910	559	430	904	546
Mass loss of Cu mg/dm² SAAB coupons							
	ISO 21207 B		Mod A		Mod B		Mod C	
Test 1 and 2	-	-	695	561	544	614	893	-

In Figure 11 mass loss results from *SP* and *SAAB* can be seen. For copper coupons the corrosion rates have increased for all tests.
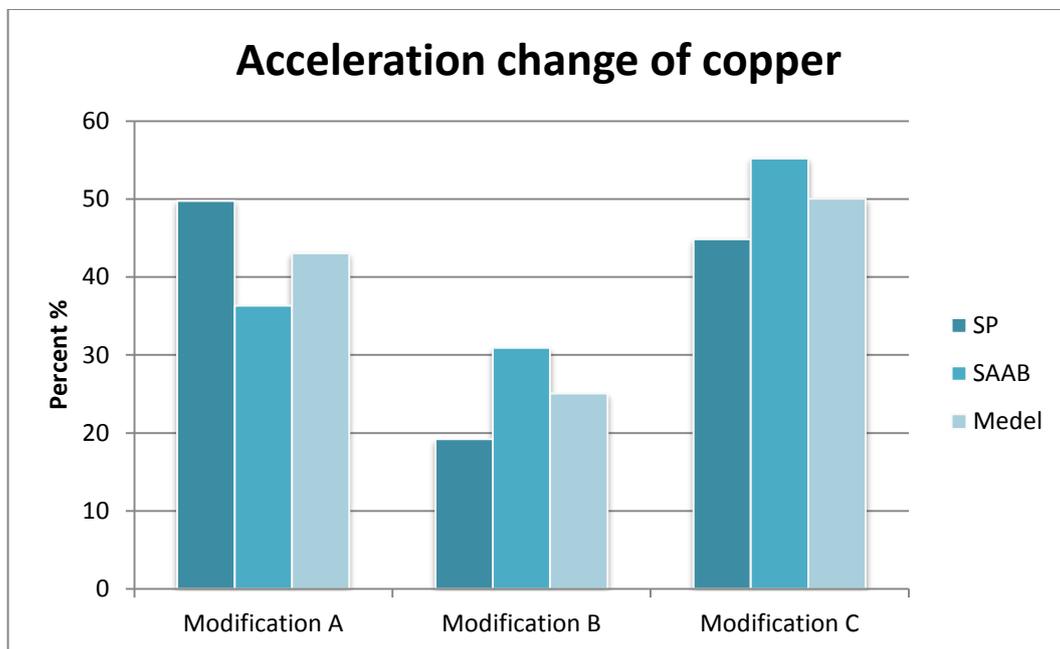

Figure 11 This bar chart describes the acceleration change in percent for all modifications for corroded copper coupons compared to the standardized method.

7.5 Mass loss of zinc

In Figure 12 zinc coupons before test and after Modification B and C are presented. No significant differences can be seen between after Modification B and C.

Figure 12 Pictures of zinc coupons before and after test ISO 21207 method B Modification B (Mod B) and Modification C (Mod C).

In Table 9 the mass loss results from *SP* and *SAAB* coupons can be seen. For zinc the corrosion rate has not increased much for the tests and in some cases even decreased.

Table 9 Mass loss results for SP zinc coupons and SAAB zinc coupons from testing methods ISO 21207 method B and Modification A, B and C (Mod A, B and C). Two tests on each modification.

Mass loss of Zn mg/dm^2 SP coupons							
	ISO 21207 B		**Mod A**		**Mod B**		**Mod C**
Test 1 and 2	750	-	834	870	622	422	842	530
Mass loss of Zn mg/dm^2 SAAB coupons							
	ISO 21207 B		**Mod A**		**Mod B**		**Mod C**
Test 1 and 2	-	-	361	380	1010	1619	1470	-

In Figure 13 the mass loss increase and decrease for zinc after test can be seen.
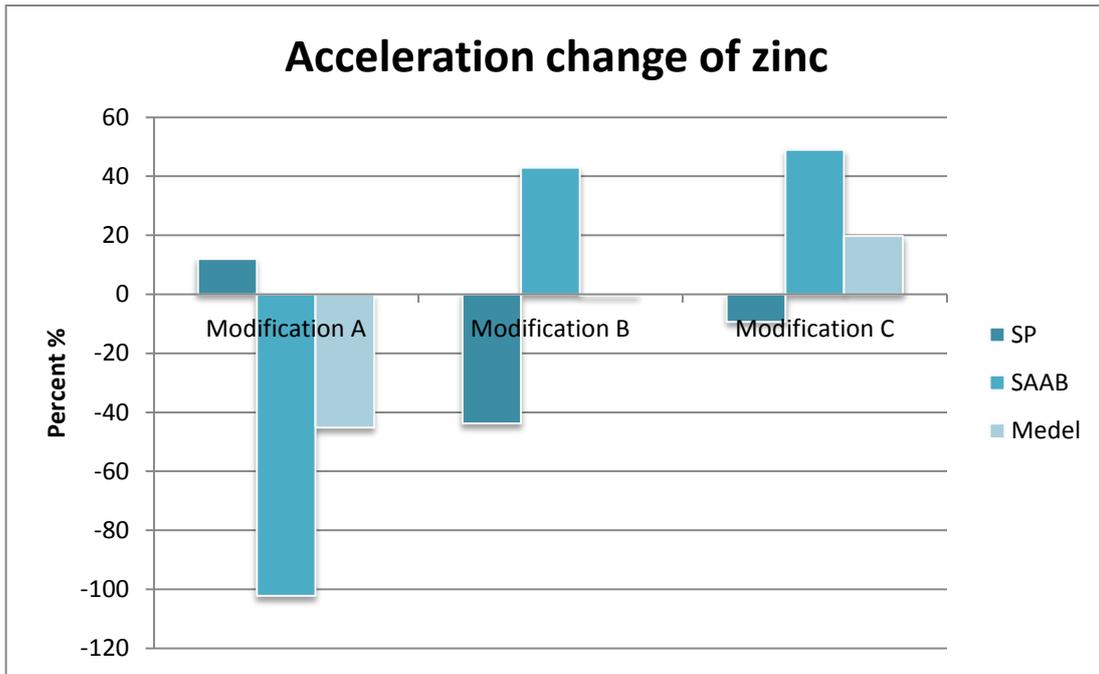
Figure 13 This bar chart describes the acceleration change in percent for all modifications for corroded zinc coupons compared to the standardized method.

7.6 IC and ICP-MS

In this section quantitative results from IC and ICP-MS are presented for aluminum and copper coupons.

7.6.1 ICP and ICP-MS results of exposed aluminum

In Table 10 the quantitative results from IC and ICP-MS for aluminum coupons are presented.

Table 10 Quantitative results from IC and ICP-MS on aluminum coupons exposed for ISO 21207 method B and Modification C. The results show only water soluble corrosion products. Oxygen in this table is calculated as a rest.

Corrosion products from Aluminum		
	ISO 21207 method B	Modification C
Chemical substance	Weight %	Weight %
Cl^-	7.0	2.6
SO_4^{2-}	3.9	8.7
$S\text{-}SO_4^{2-}$	1.3	2.9
S	7.5	8.6
Al	17	17
O	68	72

27

7.6.2 ICP and ICP-MS results of exposed copper

The weight percent from IC and ICP-MS of corrosion products on copper are presented in Table 11 for ISO 21207 method B and Modification B and in Table 12 for Modification C.

Table 11 Quantitative results from IC and ICP-MS on copper coupons from ISO 21207 method B and Modification B. The results show only water soluble corrosion products. Oxygen in this table constitutes ofis calculated as a rest.

Corrosion products from Copper		
	ISO 21207 method B	Modification B
Chemical substance	Weight %	Weight %
Cl^-	0.73	2.9
SO_4^{2-}	17	12
$S-SO_4^{2-}$	5.6	3.9
S	5.4	9.3
Cu	53	9.7
O	40	78

Table 12 Quantitative results from IC and ICP-MS on copper coupons from Modification C. Copper coupons exposed for Modification C contain two parts, one that is blue crystal like and one that is grey. The results show only water soluble corrosion products. Oxygen in this table is calculated as a rest.

Corrosion products from Copper		
	Modification C Blue crystals part	Modification C Grey part
Chemical substance	Weight %	Weight %
Cl^-	0.25	1.0
SO_4^{2-}	33	19
$S-SO_4^{2-}$	11	6.4
S	14	11
Cu	24	38
O	62	50

7.7 SEM

In this section results of quantitative analysis with SEM-EDX are shown. It is the cross section that has been analyzed since results are better when the sample is smooth, and smoothing the top layer of the panel will lead to destroyed corrosion products. The samples analyzed are copper and aluminum coupons that have been exposed to ISO 21207 method B and to Modification B and C. The weight percent of the corrosion products present are measured and shown in tables. In the SEM images the bulk and the epoxy are marked.

7.7.1 SEM-EDX of aluminum coupons

First the corrosion products of aluminum coupon exposed to the standardized method ISO 21207 method B are examined as a reference. One coupon from testing method Modification C is examined and compared to the reference aluminum coupon.

To find out what components are present at the surface of the corroded metal coupons SEM-EDX is used. From a marked place in the SEM picture a spectrum is made by EDX where the chemical elements can be seen.

7.7.1.1 Aluminum ISO21207 method B

For aluminum exposed to ISO 21207 method B the spectrum is shown in Figure 15 and corresponding SEM picture in Figure 14.
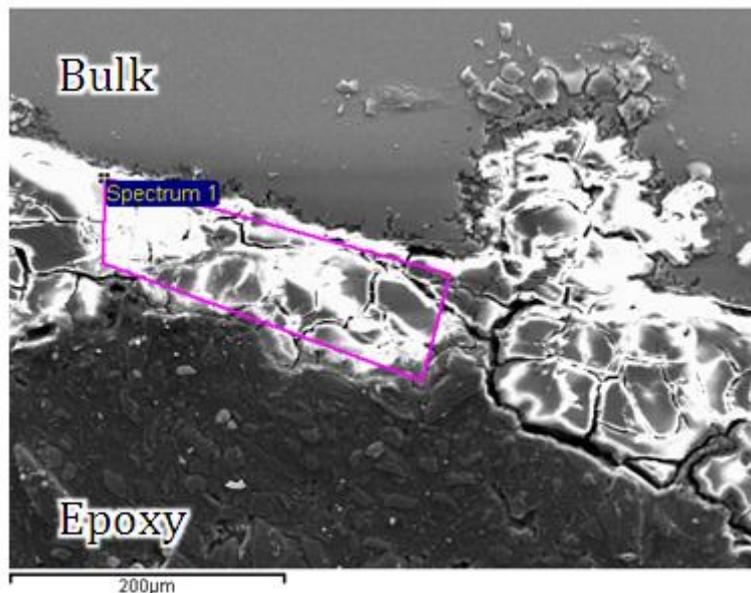
Figure 14 SEM picture of aluminum from test method ISO 21207 method B and used in EDX for spectral information. The marked section is used to create a spectrum.

From the spectrum in Figure 15 it can be seen that the surface consists of a mixture of aluminum, chloride, oxygen, sodium and sulfur. The signal from silicon is contamination and comes from the polishing process.
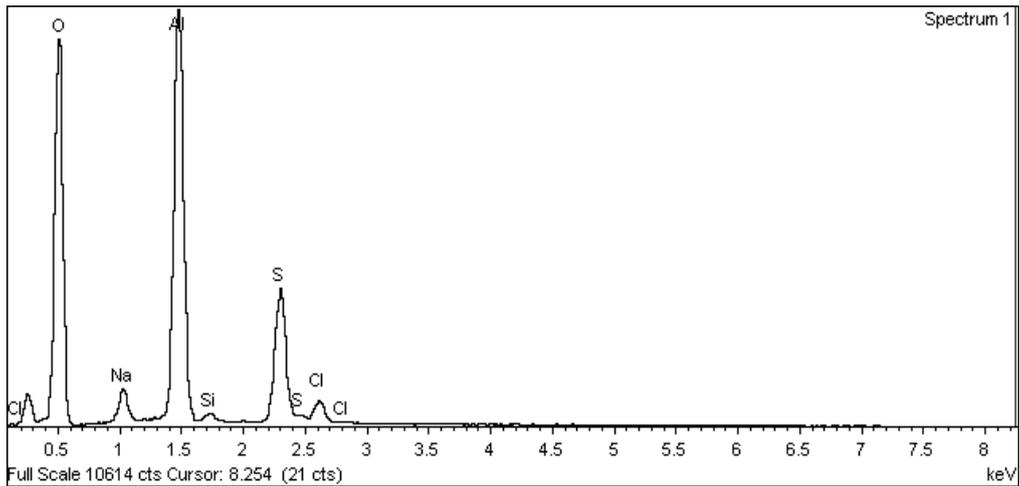
Figure 15 Spectrum of aluminum coupon tested with ISO 21207 method B.

In Figure 16 distribution of chloride and sulfur over the cross section is presented using mapping. It is the same SEM picture as in Figure 14 and in the picture to the right of Figure 16 chloride is green and sulfur is red.
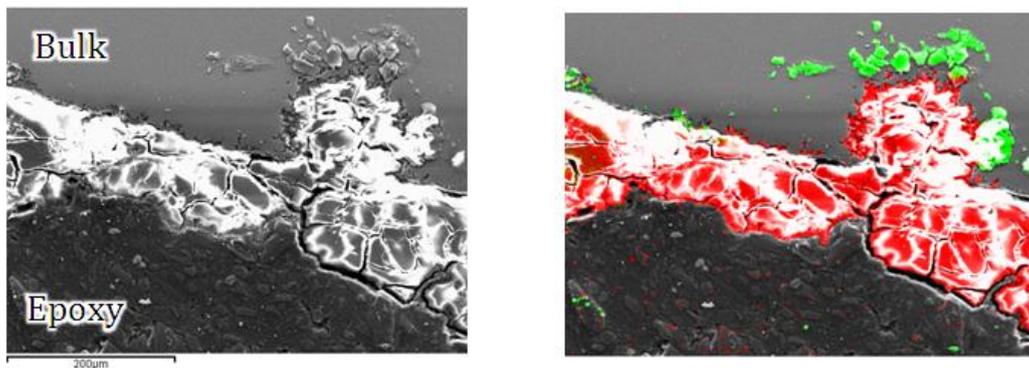
Figure 16 SEM picture of the cross section of aluminum exposed to ISO 21207 method B. The left picture shows the SEM picture and the right shows mapping of chloride and sulfur on the surface, where green is chloride and red is sulfur.

The mapping picture shows that there are more corrosion products containing sulfur than corrosion products containing chloride and the location of chloride is closer to the bulk.

7.7.1.2 Aluminum Modification C

SEM electron image of aluminum coupon exposed to Modification C is shown in Figure 17. The chemical element information is shown in the spectrum in Figure 18.
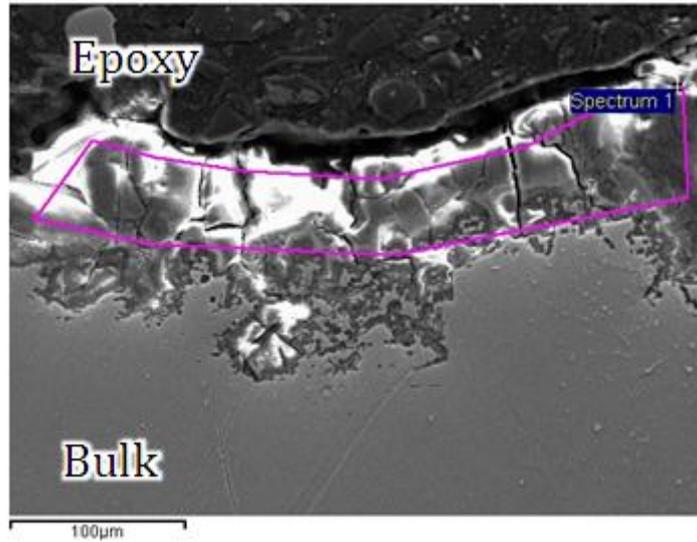
Figure 17 SEM picture of the cross section of aluminum coupons exposed to Modification C.

The spectrum in Figure 18 shows the same elements as in Figure 15.
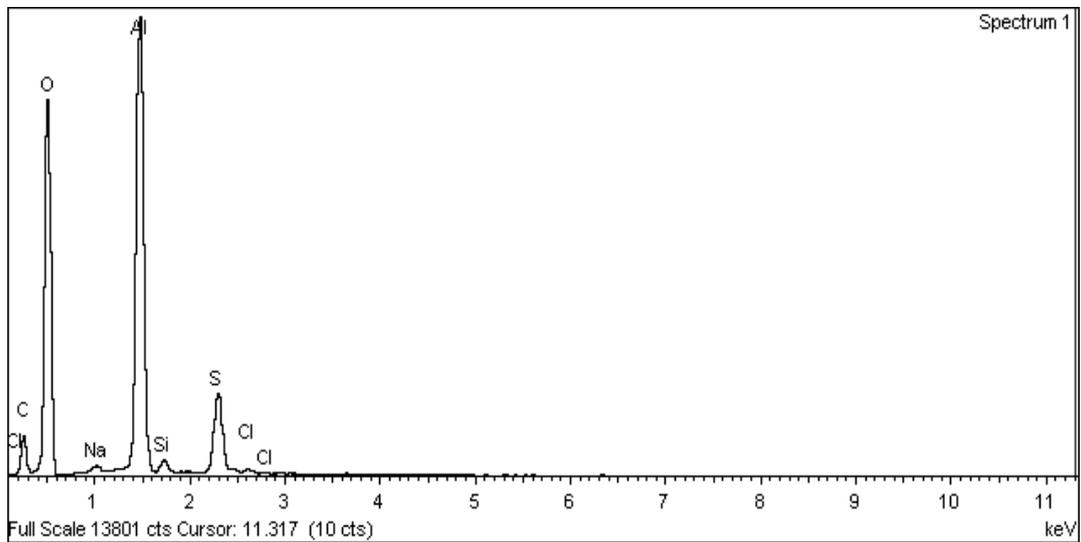
Figure 18 Spectrum for aluminum exposed to Modification C.
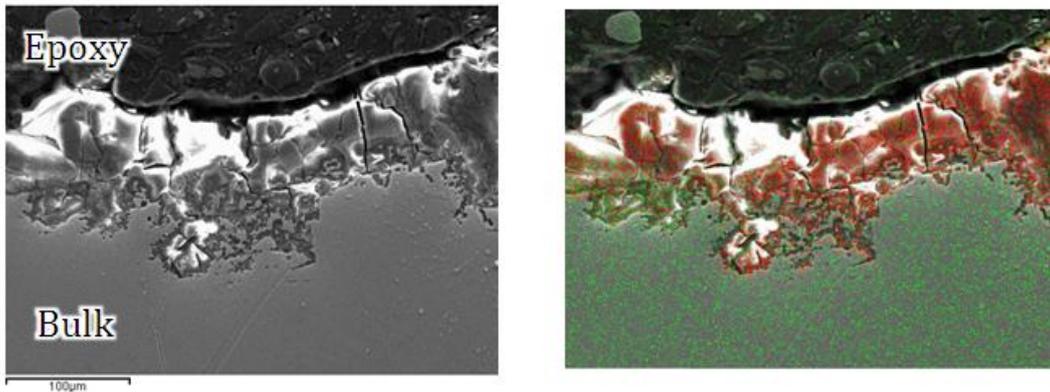
Figure 19 Mapping of aluminum that has been exposed to the corrosive species in Modification C. In the right picture green is chloride and red is sulfur, but it must be noted that green in the bulk does not consist of chloride but is due to equalization.

7.7.2 SEM-EDX of copper

The corrosion products of copper coupons have been analyzed with SEM-EDX. The analyzed copper coupons have been exposed to ISO 21207 method B, Modification B and Modification C. The first sample is copper coupon exposed to ISO 21207 method B and acts as reference. That result is compared with results from Modification B and C.

7.7.2.1 Copper ISO 21207 method B

A SEM picture of copper coupon tested with ISO 21207 method B is presented in Figure 20 and the corresponding spectrum from the marked area in Figure 21.
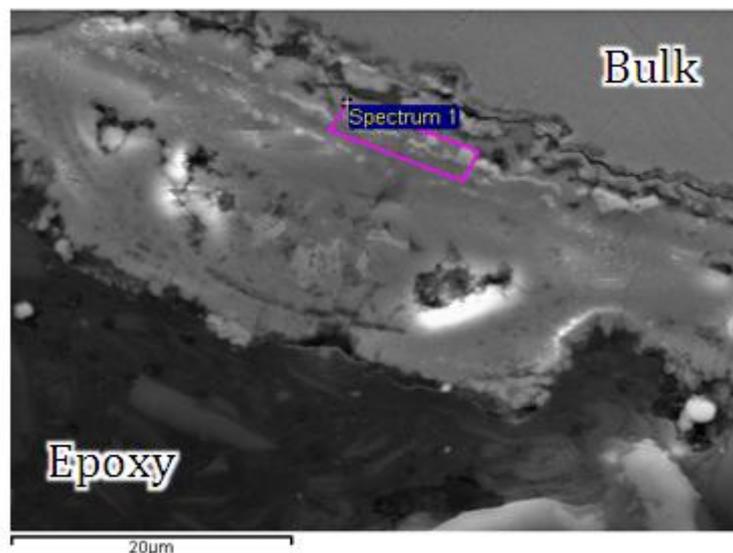
Figure 20 SEM image of the corrosion products of copper exposed to the standardized test method ISO 21207 method B. The marked area corresponds to the spectrum in Figure 21.

From Figure 21 it can be seen that the copper surface consists of chloride, oxygen and sulfur.
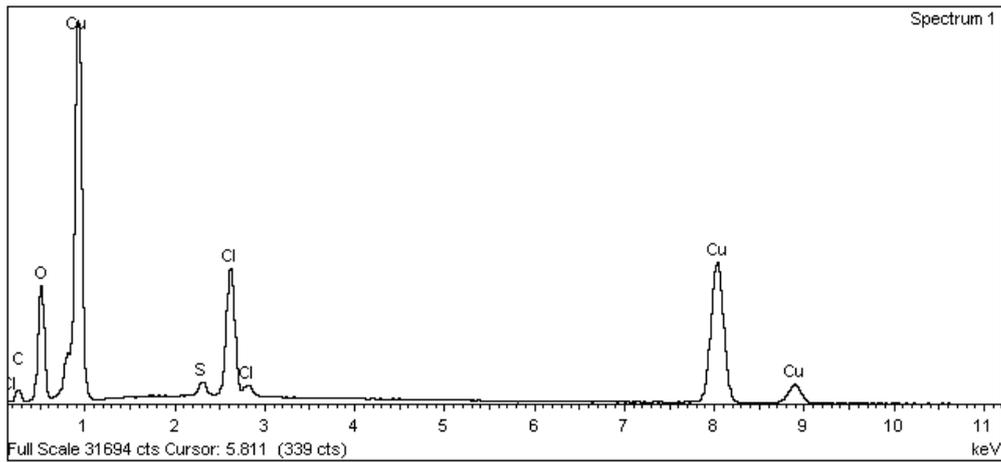
Figure 21 Spectrum for copper tested with ISO 21207 method B.

From the mapping in Figure 22, it can be seen that chloride and sulfur come as layer. The first layer nearest the bulk consists of chloride and is covered by a sharp layer of sulfur.
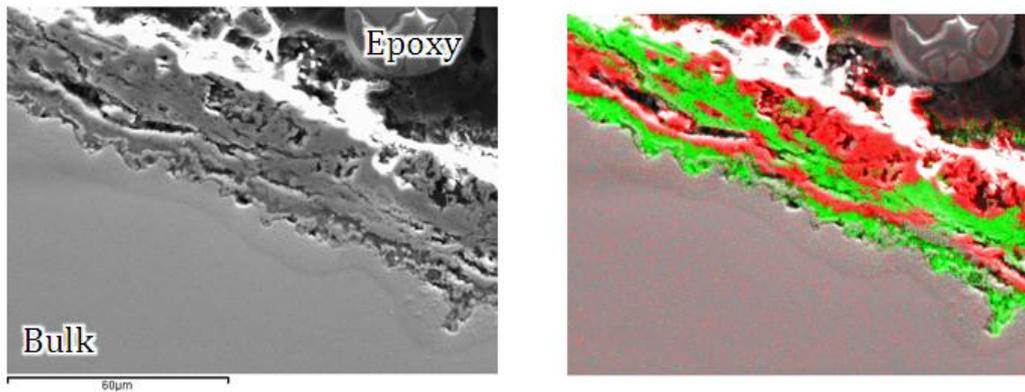

Figure 22 Mapping of the corrosion products on copper from the standardized method ISO 21207 method B. On the right picture green is chloride and red is sulfur.

7.7.2.2 Copper Modification B

SEM picture of copper exposed to the corrosive species in *Modification B* is presented in Figure 23 and corresponding spectrum in Figure 24.

Figure 23 Cross section of copper coupon that has been exposed to Modification B.

The spectrum shows almost the same results as for copper exposed to ISO 21207 method B. The surface consists of chloride, copper, oxygen and sulfur but also a very small peak of nitrogen can be distinguished. The peaks of silicon and carbon are contamination and come from the polishing process.
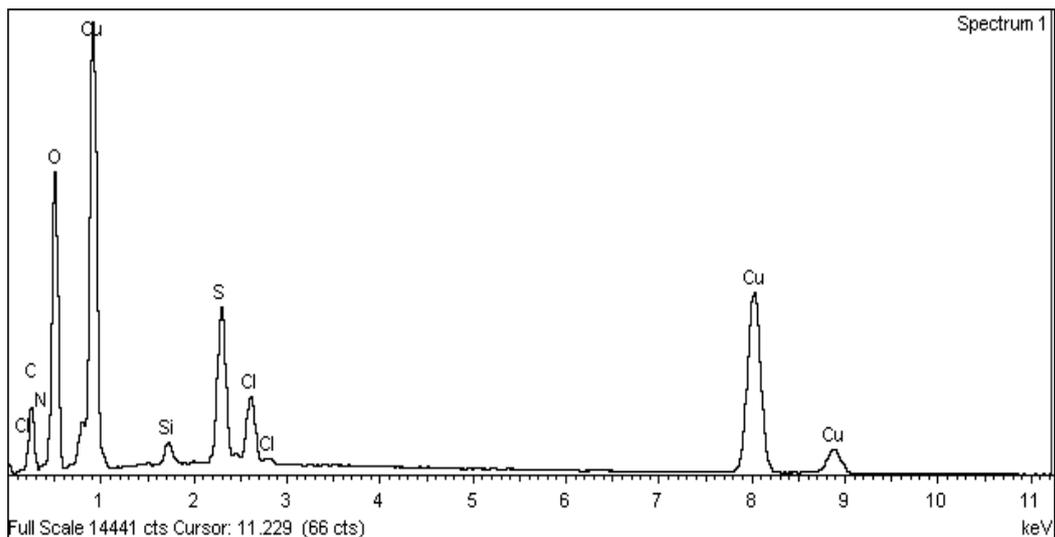
Figure 24 Spectrum from copper that has been exposed to test method Modification B.

SEM mapping results show layer formation of chloride and sulfur.
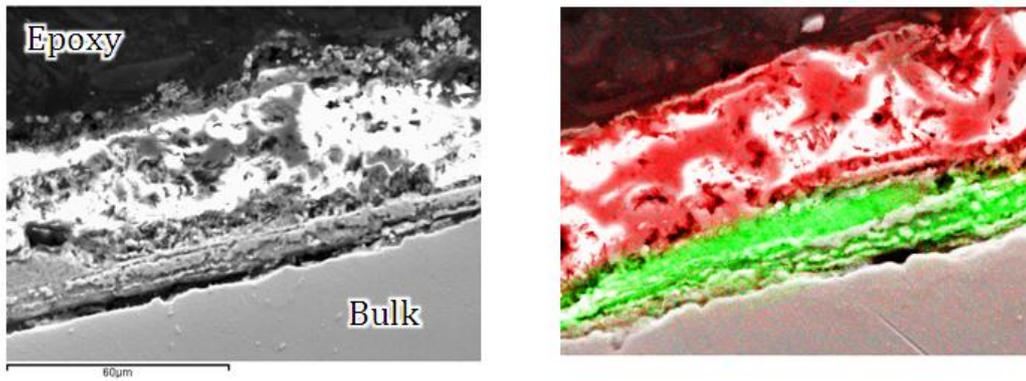
Figure 25 Mapping image of copper that have been exposed to Modification B. On the right picture green is chloride and red is sulfur.

7.7.2.3 Copper Modification C

A SEM picture of copper coupon that has been tested with Modification C is presented in Figure 26. The corresponding spectrum for the marked area is shown in Figure 27.
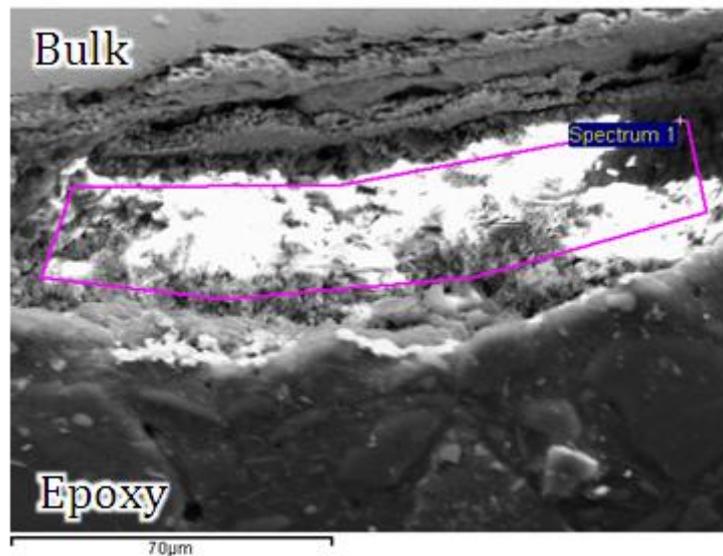
Figure 26 SEM image of the corrosion products on copper from Modification C.

The peaks in Figure 27 show the same elements as for the copper coupons tested with ISO 21207 method B and Modification B. Unfortunately the peak of chloride cannot be seen but is located to the left in the picture.
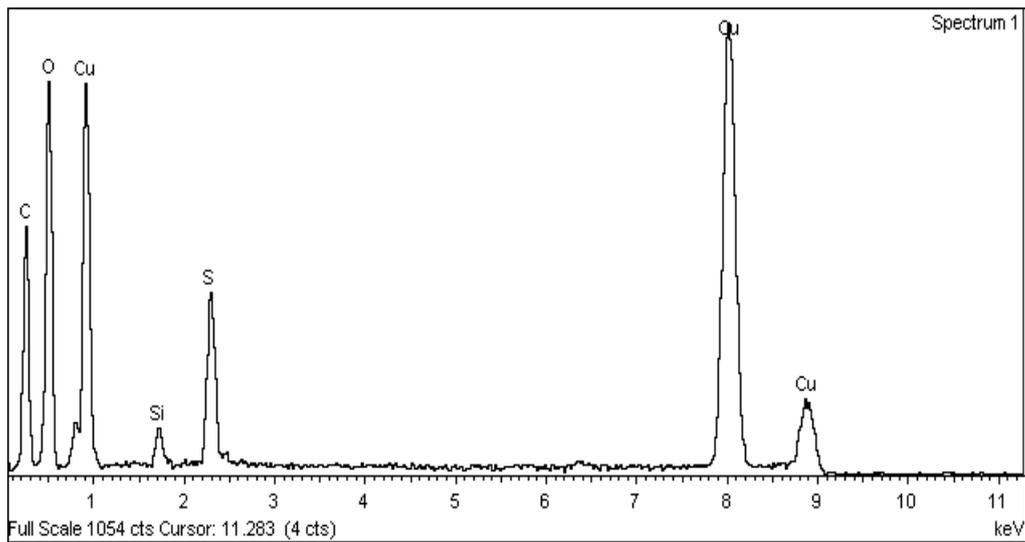
Figure 27 Spectrum of the corresponding SEM image Figure 26.

The mapping for copper from Modification C also shows layer formation from chloride and sulfur and this is pictured in Figure 28.
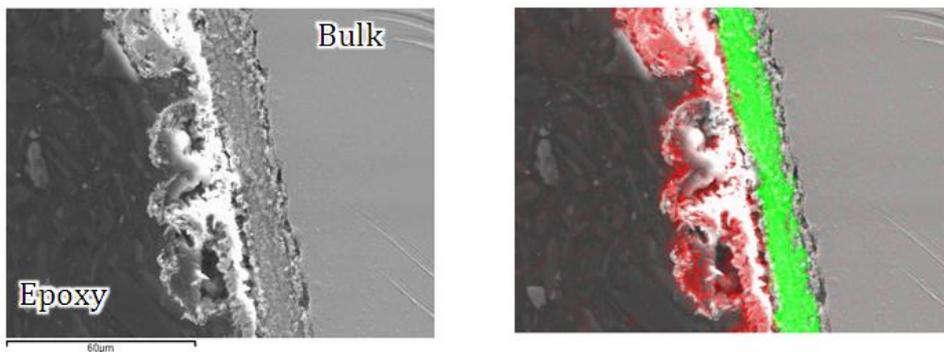

Figure 28 Mapping of copper coupon that has been tested with Modification C.

7.8 XPS

In this section survey spectra from analysis from XPS of aluminum and copper coupons are presented. These spectra are compared for identification of differences on the coupon exposed to different testing methods.

7.8.1 XPS survey spectrum for exposed aluminum coupons

The survey spectra for aluminum coupons from ISO 21207 method B and Modification C are presented in Figure 29. In the survey spectra there are peaks of aluminum, chloride, oxygen, nitrogen, sodium and sulfur.
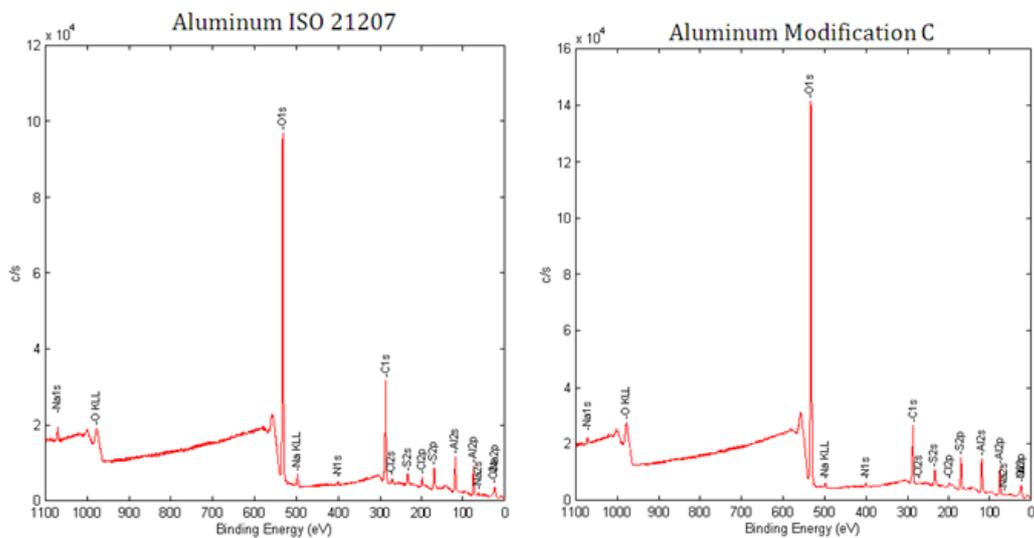

Figure 29 Survey spectra of aluminum coupon tested with ISO 21207 method B to the left and Modification C to the right.

7.8.2 XPS survey spectrum for exposed copper coupons

Survey spectra for copper coupon exposed for ISO 21207 method B, Modification B and Modification C are shown in Figure 30. The spectra show peaks of chloride, copper, oxygen, sodium and sulfur.
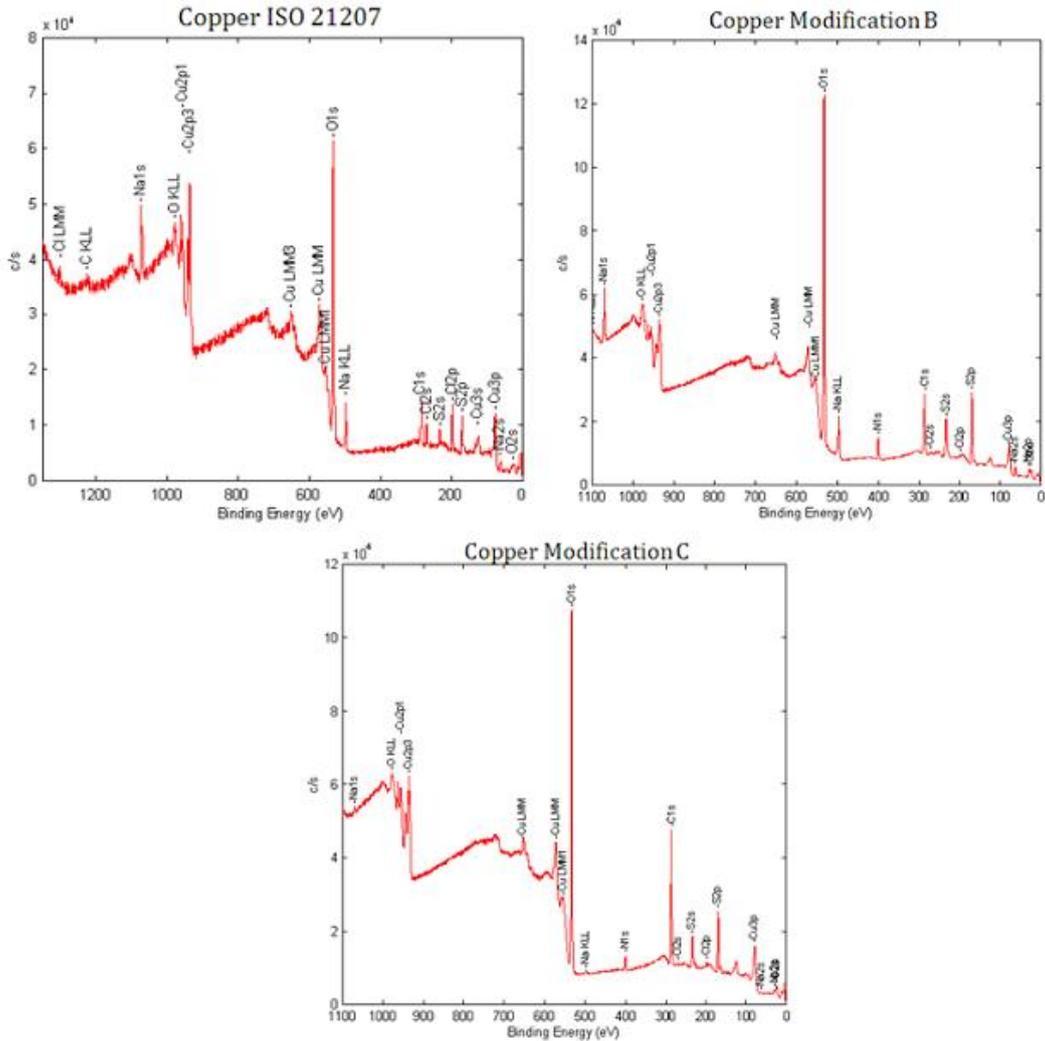

Figure 30 Survey spectra of copper coupon tested with ISO 21207 method B, Modification B and Modification C.

7.9 XRD

In this section results from XRD analysis are presented for aluminum and copper coupons.

### 7.9.1 X-ray diffractogram for exposed aluminum coupons
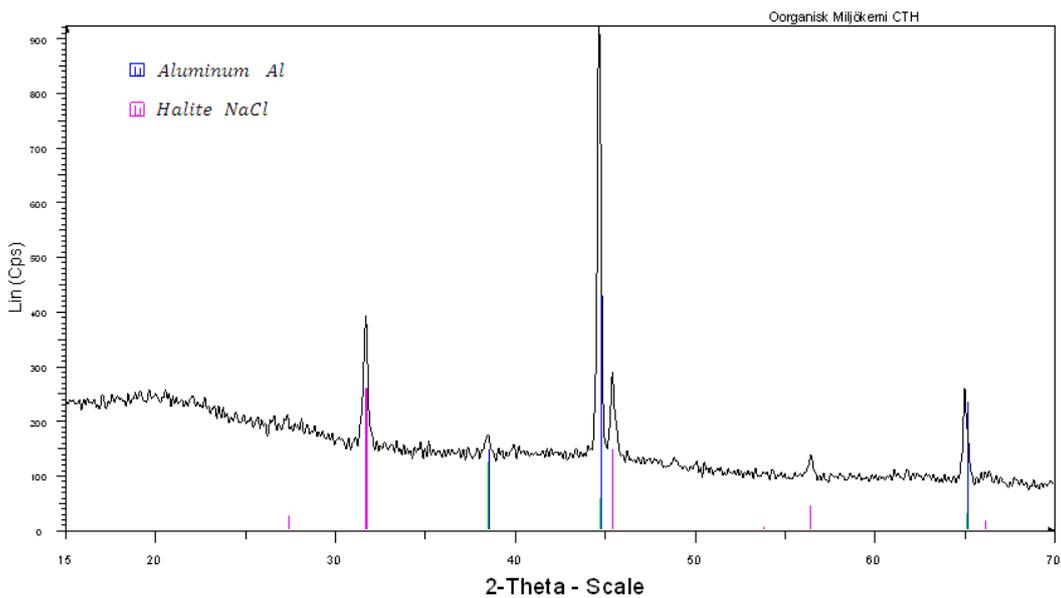
**Figure 31 X-ray diffractogram of aluminum coupon exposed to ISO 21207 method B.**
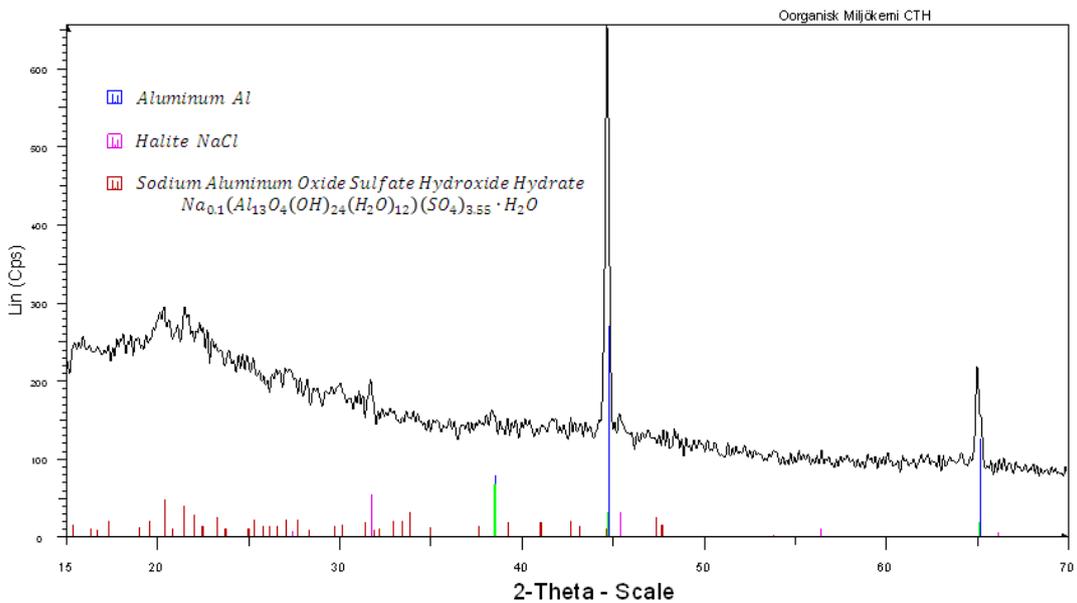
Figure 32 X-ray diffractogram of aluminum coupon exposed to Modification C.

## 7.9.2 X-ray diffractogram for exposed copper
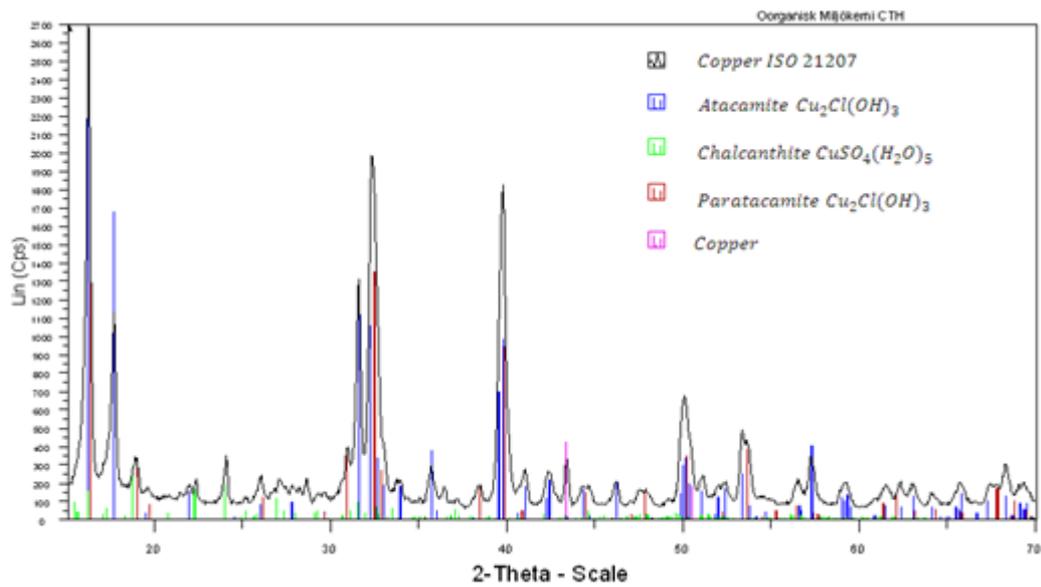
Figure 33 X-ray diffractogram of copper coupon exposed to ISO 21207 method B.
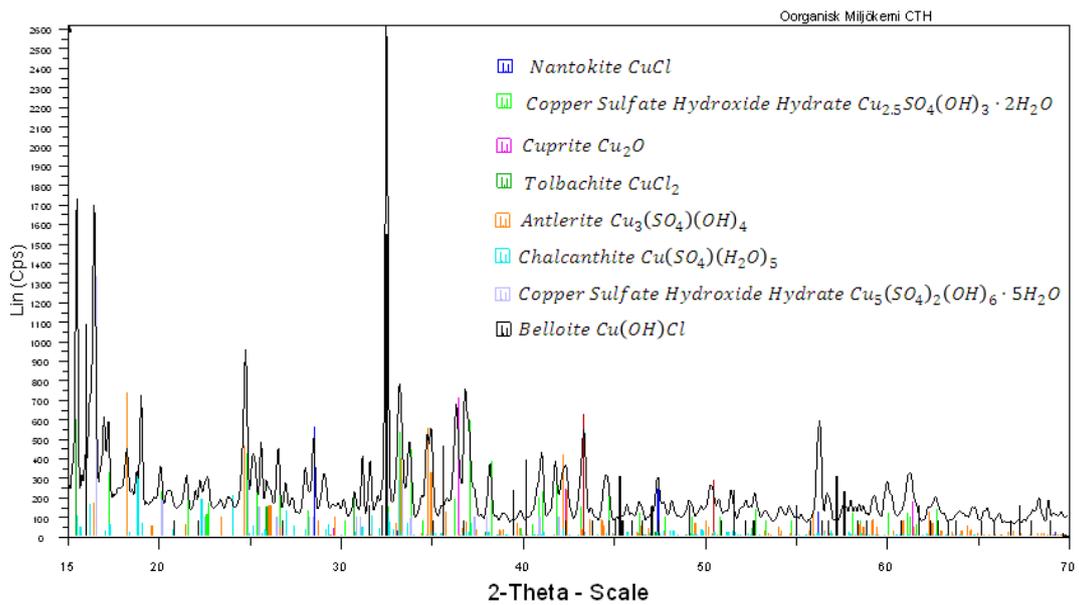

**Figure 34 X-ray diffractogram of copper coupon exposed to Modification B.**
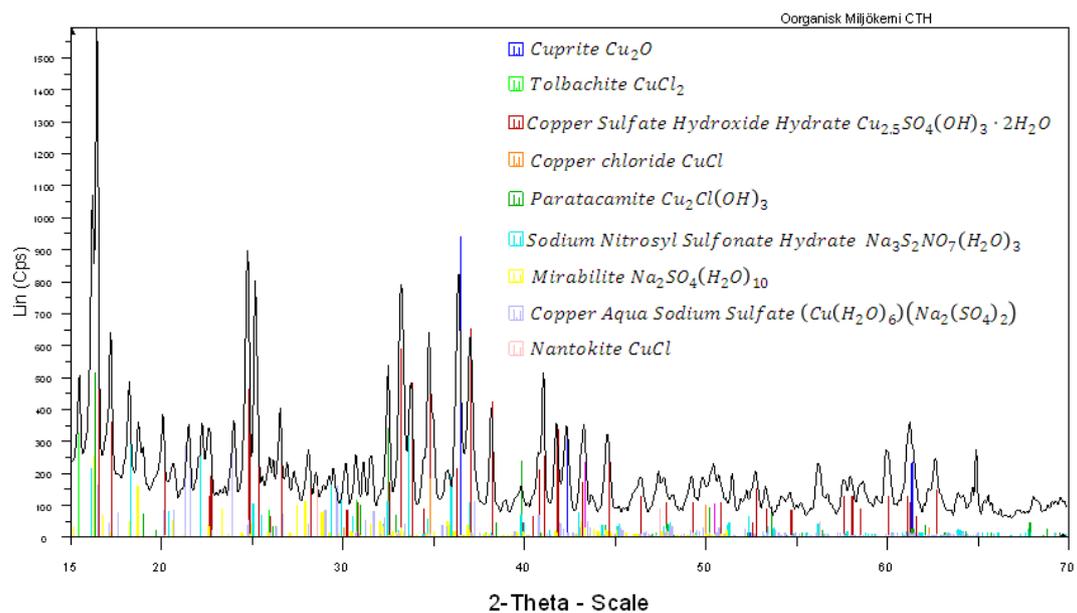
Figure 35 X-ray diffractogram of copper coupon exposed to Modification C.

8 Discussion

The wanted outcome from the mass loss results is an accelerated corrosion rate over 40%. The most important factor is though not to change the type of corrosion products when changing the acceleration factor.

From the mass loss results of aluminum it can be seen that the corrosion rate has increased over 40% in all tests at *SP*. But for *SAAB* the increase compared to the original method ISO 21207 method B is less, and in the case of Modification B there is even a decrease of mass loss compared to the original method. Overall for aluminum the corrosion tests are tougher at *SP* than at *SAAB*. One aspect is that corrosion of aluminum can be strongly affected with temperature (N.Lampeas, 1994). But the standard does specify the temperature so this may not be the problem in this case.

For carbon steel the corrosion rate has increased over 40% in all tests at *SP* but for *SAAB* the increase is less than 40% and in the case of Modification A the mass loss has decreased compared to the standardized method. The differences in mass loss results for *SP* and *SAAB* can depend on how the hostile gases SO_2 and NO_2 are distributed in the chamber. The corrosion rate on carbon steel is strongly dependent on the flow rate of the hostile gases.

In the case of copper every modification accelerated the corrosion rate compared to the original method both at *SP* and *SAAB* but for *SAAB* the increase was never over 40%. Only small differences in the mass loss results between *SP* and *SAAB* compared to the other metals could be observed. This can be because the standardized method is developed for copper and the corrosion on copper is more uniform. The corrosion products at low pH around 3 for copper can lead to formation of porous corrosion products (Y. Feng, 1997). In acidic solution such as hydrochloric acid copper has limited utility due to sensitivity to aeration, velocity and oxidizing impurities (Crum, 2011).

In the case of zinc, the corrosion rate only increases in one case. Moreover, there are significant differences between mass loss results for *SP* and *SAAB*. One explanation can be that neutral salt spray is more corrosive than salt spray at low pH for zinc. Some of the corrosion products on zinc may be conductive which increases corrosion in contact with salt.

One reference in the literature says that corrosion weight loss increases with decreasing pH lower than 3.5 for zinc (M. Shinichi, 1999). The short time salt spray at low pH exposure in this thesis may be an explanation of zinc results.

The differences of corrosion rate for *SAAB* versus *SP* are distinct. The testing methods used are the same, there were only performed at different locations with different equipment. The testing environment at SP seems to be more severe than at *SAAB*.

Metals can be sensitive for how they are exposed in the climate chamber. At *SAAB* they use a fan is used in the climate test chamber for hostile gas exposure and this is not done at *SP*. Two metals that are sensitive for how the hostile gases are distributed are iron and zinc. However the fan used in the climate chamber at *SAAB* could lead to a lower concentration of hostile gases at the metal surfaces which may lead to a decrease in corrosion rate. The ISO standard do specify the flow rate of SO_2 and NO_2 so this should not be a difference at *SP* and *SAAB*

From the results from IC for aluminum coupons it can be seen that the surface may include other species that contain sulfur. This result can be seen for both ISO 21207 method B and Modification C.

SEM analysis of aluminum coupons tested with ISO 21207 method B and Modification C shows that the surface of the coupons contains the same elements for both tests. The mapping revealed that the amount of chloride is small and that chloride appears closer to the bulk. The polishing process of the cross section of the corroded aluminum sample is difficult since the porous corrosion products can easily be damaged and fall of.

The SEM results for copper coupons show corrosion products containing chloride and sulfur at the surface. With ISO 21207 method B the distribution of chloride and sulfur comes as layers. This layer formation can be due to the cyclic process.

Interpretation of the sulfur peak in the ESCA results was difficult. The peak is located at a high shift around 169 eV and this can indicate SO_4^{2-} at the surface. The chloride peak is distinct and indicates Cl^- at the surface. The ESCA survey spectra for aluminum coupons exposed to ISO 21207 method B and Modification C are similar which can mean that the increased corrosion rate has not changed the corrosion products significantly. The same results from the survey spectra from copper can be seen.

The results from XRD for aluminum coupons exposed to ISO 21207 method B and Modification C gave specific chemical compounds in the corrosion products. One chemical compound, sodium aluminum oxide sulfur hydroxide hydrate, is added when

exposed to Modification C compared to when exposed to ISO 21207 method B. Overall XRD analysis of aluminum coupons indicates of few corrosion products and a reason can be that the corroded surfaces of aluminum only consists of amorphous products.

The surfaces of corroded copper coupons consists of crystalline products thereof better results from XRD. When comparing the results for copper coupons exposed to ISO 21207 method B, Modification B and Modification C it can be observed that the corrosion products are depending on which test method used. The amount corrosion products tend to increase when comparing the standardized method with Modification B and Modification C.

One reason why the corrosion products are changing when decreasing the pH can be that HCl acts as a pickling agent and then cleans the metals. When decreasing the pH with HCl one corrosion product on copper is $CuCl_2$, as seen on the results from XRD. Changing the pH decreasing agent to H_2SO_4 could be an alternative in order to avoid formation of new chemical compounds compared to the original method.

9 Conclusions

In this project a method for service lifetime prediction for electronics ISO 21207 method B is used, and this method has been developed by *SP Technical Research Institute of Sweden*. The aim was to accelerate the standardized method with a factor of 40% by three modifications. After test following conclusions are made:

- The corrosion rate has increased with 40% for copper which means that the goal has been reached.

- Low pH during salt spray exposure gives no significant differences in increasing the corrosion rate compared to increasing the concentration of gas.

- The combination of low pH and high concentration of gas is changing the corrosion products and can be seen both visually and by XRD.

- The corrosion products on copper form layers of chloride and sulfur due to the cyclic test method.

- HCl can act as a pickling agent in the salt spray.

10 Future work

For future research in this area surface analysis of corroded copper from tests with increased quantity of gas should be analyzed, in order to find out the differences in corrosion products compared to the other modifications.

All other metals that have not been surface analyzed in this thesis could be analyzed in a new research project. Zinc behavior is very interesting due to no pattern when being exposed to low pH.

The differences between the results from *SP* and *SAAB* could also be further investigated. The differences are significant even though the same test methods and ISO standard are used.

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