Corrosion inhibitor screening for galvannealed steel and high-strength steel

Master Thesis
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Corrosion inhibitor screening for galvannealed steel and high-strength steel

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Corrosion on the car underbody can affect critical parts, which poses safety risks. The current corrosion protection methods such as wax, sealers and coatings are not effective enough and an advance form of corrosion protection is desired. Implementation of smart coatings might be an effective solution. These coatings contain a self-healing agent which is released when damage to the coating occurs. Corrosion inhibitors can be used as such self-healing agents. However, to implement them an effective inhibitor must be found first. The present study will search for an effective inhibitor for the protection of the car underbody metals: galvannealed steel and high-strength steel. Initially, an inhibitor screening was applied, which resulted in sodium metasilicate being the most potent inhibitor. This inhibitor was further studied with adsorption isotherm models, SEM & EDS, FTIR, LSV and EIS. The results from these experiments suggest that sodium metasilicate protect its substrate by forming a protective silicate layer which protects the substrate from corrosion. Furthermore, it appears that this layer differs in properties depending on which substrate it is used.

Keywords: corrosion, GA steel, HSS, smart coatings, inhibitors, screening, adsorption isotherm, SEM, EDS, FTIR, LSV, EIS
Contents

1 Introduction
  1.1 Objective and approach thesis .............................................. 2

2 Background
  2.1 The car underbody .......................................................... 3
    2.1.1 Galvannealed steel .................................................... 4
    2.1.2 High-strength steel ................................................... 5
  2.2 Current corrosion protection methods ..................................... 6
  2.3 Inhibitors .......................................................................... 8
  2.4 Smart coatings .................................................................... 11
    2.4.1 Self-healing principle ................................................... 11
    2.4.2 Smart coatings for car underbody ................................. 14
  2.5 Summary ............................................................................ 15

3 Methods & Experimental ....................................................... 17
  3.1 Principles of analysis techniques used in this work. ................ 17
    3.1.1 Surface analysis .......................................................... 17
    3.1.2 Electrochemical analysis ............................................... 21
  3.2 Experimental .................................................................... 27
    3.2.1 Materials .................................................................... 27
    3.2.2 Electrochemical studies ............................................... 27
    3.2.3 Inhibition performance in time study ............................ 28
    3.2.4 Surface analysis .......................................................... 28

4 Screening of corrosion inhibitors ............................................ 29
  4.1 General corrosion mechanisms substrates .............................. 29
    4.1.1 Galvannealed steel ....................................................... 29
    4.1.2 High-strength steel ...................................................... 30
  4.2 Literature review of corrosion inhibitors for GA steel and HSS .... 30
  4.3 Electrochemical performance screening .................................. 41
    4.3.1 Polarisation curves ....................................................... 41
    4.3.2 Inhibitor efficiencies .................................................... 44
    4.3.3 Final inhibitor selection ............................................... 49
  4.4 Conclusions ..................................................................... 51

5 Corrosion inhibitor mechanism study ..................................... 53
  5.1 Research approach ............................................................ 53
  5.2 Adsorption isotherms ........................................................ 54
  5.3 Surface analysis ............................................................... 57
    5.3.1 SEM & EDS measurements ........................................... 57
    5.3.2 FTIR measurements ..................................................... 64
  5.4 Electrochemical analysis .................................................... 72
    5.4.1 LSV measurements ...................................................... 72
    5.4.2 EIS measurements ....................................................... 78
  5.5 Proposed inhibition mechanism ........................................... 86
6 Conclusions 87
7 Recommendations 89
A Appendix A 91
A.1 LSV plots 91
A.1.1 GA steel 91
A.1.2 HSS 95
A.2 Pourbaix diagrams 98
B Appendix B 101
B.1 SEM & EDS 102
C Appendix C 103
C.1 FTIR spectra 104
C.1.1 GA steel 104
C.1.2 HSS 106
C.2 FTIR surface measurement 108
Bibliography 109
Corrosion, has one of the biggest costs impacts on nowadays economy, estimated at almost 4% of the Gross Domestic Product (GDP). This figure does not even include cost due to environmental impact, loss of product, plant downtime, etc. [2]. Many industries therefore try to minimize the effects of corrosion. The automotive industry represents one of those industries. Here, a lot of costs are involved to guarantee consumers no visible corrosion occurs. Consumers tend to avoid cars which have red rust spots on their interior or exterior parts, which will affect sales and the image of the car brand. Car magazines can, for example, write bad reviews about the car based on the observed corrosion.

Besides the financial stakes and the image of the brand, corrosion also poses safety risks. Holes caused by corrosion can affect structural integrity and therefore safety. One of the more critical parts of a car is the underbody, here many structural parts lie, such as the suspension members, oil tanks and the floor. Damages occurring in this area can cause life threatening dangers. The underbody must endure a variety of attacks from the environment. Stone chipping, mud and de-icing salts can deteriorate the underbody of the car during regular use [3]. Furthermore, the underbody must endure climate change during regular usage. For example, imagine a car in Italy driving to Spain. The car in Italy will initially face marine conditions while as it continues in Spain in a dry conditions. Obviously one could expect more corrosion in the marine environment than the dry environment.

To protect the underbody, cars are usually protected by a variety of methods. Current protection methods involve wax, sealers, covers and coatings. Especially the latter is extensively used in automotive industry. Coatings protect the metallic substrate by separating it from its environment and therefore prevent corrosion. Despite their effectiveness, they still can degrade in time. Mechanical defects can occur, such as scratches caused by stone chipping. Due to the unavoidable permeability of coatings, water can also penetrate the coating due and reach the surface below, initiating corrosion.

To increase corrosion resistance, a more advanced form of corrosion protection is desired. This next step involves the implementation of a so-called smart coating. These coatings contain a healing agent, which are released when damage to the coatings occurs, actively repairing the damage. The implementation of these smart coating might extensively increase the lifetime of the underbody.

To develop these kinds of coatings, the healing agent must be developed. Here, this will involve the use of corrosion inhibitors, chemicals that retard corrosion. Unfortunately, these types of chemicals are highly specific and will might not have the same effectiveness on a different substrate. Therefore, an intensive screening process is usually required based on trial-and-error.

In short, corrosion on the car underbody affects critical parts, which poses safety risks. The current corrosion protection methods are not effective enough and an advanced form of corrosion protection is desired. Smart coatings might be an effective solution. However, to implement them an effective inhibitor must be found first.
1. Introduction

1.1. Objective and approach thesis

In the present work, goal is to obtain an effective inhibitor for the car underbody metals; galvannealed steel and high-strength steel. The approach is divided into two parts: the corrosion inhibitor screening and the inhibition mechanism (see figure 1.2). In chapter 4, a literature screening is applied, which gives a comprehensive list of potential candidates. To narrow down this list, additional selection criteria are applied. An electrochemical evaluation is followed, which eventually will give rise to the best inhibitor. In chapter 5, its corrosion mechanism is studied with surface analysis, adsorption models and electrochemical analysis.

Figure 1.2: The approach of obtaining an effective inhibitor for the car underbody metals
In this chapter, the corrosion problems of the car underbody and the currently used corrosion protection methods for it will be briefly explained. Those current methods are not adequate enough and therefore a state-of-the-art protection method is desired: smart coatings. A key component of these materials are inhibitors, which will be discussed in more detail as well in this chapter.

2.1. The car underbody

In the automotive industry many problems exist and corrosion is one of those problems. A major problem is the possibility that components can fail due to corrosion. In worst case scenarios, this can severely affect safety of the passenger. A somewhat minor problem is the loss of aesthetics, which do not appeal to consumers. This could eventually negatively affects sales and the image of the car brand.

Especially the underbody of the car is sensitive to corrosion. There are several reasons why the underbody is the most prone to corrosion. Firstly, the underbody has many necessary design flaws such as hem flanges, crevices and holes where dirt or debris can accumulate. When wetted, this becomes a highly corrosive liquid, which can contain sodium, magnesium, calcium, chlorides and sulphates. When the metal surface is continuously exposed to this liquid, crevice corrosion can eventually occur [5]. Spot welding is also standard in car designs and is used to fix panels to each other, but can also be an area to initiate corrosion [6].

Secondly, cars are made to be sold globally and not made to be sold in a specific country. Therefore, cars must be able to adapt to various (harsh) environments. If one takes Europe as an example, one can encounter many forms of terrain and climates. Spain has deserts and mountains with rocky terrain, Italy has a warm, damp climate, in Sweden heavy snowfall can be encountered and in the Netherlands it frequently rains. The car and especially the underbody must endure all of these. Besides climate and terrain derivations, road conditions, especially stone chipping [3], poses serious problems. When stones appear on the road and they hit the moving wheels of the car, there is a chance it will be launched at the underbody. The impact might chip away part of the protective coating, exposing the bare metal.

Finally, corrosion can be accelerated in the winter, when de-icing salts are used on the road. The salts, generally, NaCl, MgCl₂ and CaCl₂, are used to depress the formation of ice. Dissolved in water, these salts form a corrosive medium. If this medium is splashed up while driving the car, it can come in contact with the bare metal parts, accelerating corrosion [7].
The underbody has a few key structures, namely the floor, the suspension members and the fuel inlet pipe (see figure 2.1). The floor of the car, made of galvannealed (GA) steel, is the foundation on which the other structural parts lies (i.e. doors, seats). The suspension is the system of tires, tire air, springs, shock absorbers and linkages that connects a vehicle to its wheels and allows relative motion between the two. The purpose of the suspension members, made of High-Strength steel (HSS), is mainly for structural reinforcement. The fuel inlet is not covered in this study, because the floor and the suspension members have a higher priority.

2.1.1. Galvannealed steel

A frequently used steel in the automotive industry is hot-dip galvanized (HDG) steel with zinc. The zinc provides the steel protection in the form of a physical barrier layer and cathodic protection. The galvanizing process first starts with the steel component being pickled and fluxed to remove grease and scale. Next, the component is immersed in a bath of molten zinc at 450-460°C [9]. This will give the substrate a uniform zinc layer with a thickness of around ten micrometer. The zinc is metallurgically bonded to the steel by forming four Zn-Fe phases; γ (75% Zn, 25 % Fe), δ (90% Zn, 10% Fe), ζ (94% Zn, 6% Fe) and η (100% Zn) [10, 11]. The zinc layer formed is usually harder than the steel substrate and therefore provides additional protection against abrasion [12]. To prevent accumulation of the pickling agent, fluxes and liquid zinc, it is usually required that the component has some holes from which the liquids can flow out.

By applying an annealing step at ≈ 540°C [9] directly after the HDG process, one creates galvannealed steel. This annealing step allows diffusion of iron into the zinc layer, alloying the zinc with 10% iron. The layer also contains small traces of aluminum to increase coating adhesion. Just as with galvanizing, the galvannealed layer can be split in distinct phases: ζ FeZn13 (5.2-6.1% Fe), δ FeZn10 (7.0-11.5% Fe) and γ Fe3Zn10 (15.8-27.7% Fe) (see figure 2.2) [13]. The resulting layer is harder due to solid-solution strengthening and is more resistant to spot welding. Furthermore, the annealing step gives the metal a rough
2.1. The car underbody

greyish matt finish, which improves paint adherence. However, the iron in the zinc layer can still corrode. This might cause a light cosmetic reddish colour, which can be prevented with a paint job [12].

![SEM cross section of galvannealed steel zinc layer.](image)

Figure 2.2: SEM cross section of galvannealed steel zinc layer. Figure reproduced from GalInfo [13].

The Pourbaix diagram for the zinc layer can be seen in figure 2.3. For the underbody corrosion, it is assumed that the aqueous medium has a neutral pH and is aerated. The top red dashed line represents the oxygen reduction line and generally, the potential lies near this line when the aqueous medium is aerated. If a line is drawn from pH 7, we can see that the zinc layer lies in the Zn$^{2+}$ and Fe$_2$O$_3$(s) stable region. Thus zinc is unstable and will dissolve to form Zn$^{2+}$. The iron present in the layer will react with oxygen to form the iron oxide. If we go near the bottom red dashed line (the hydrogen evolution line, when the medium has poor access to oxygen), zinc and iron are both dissolving. Only at lower potentials the zinc layer is immune to corrosion.

![Pourbaix diagram of a galvannealed steel zinc layer (90% Zn, 10%Fe) in water.](image)

Figure 2.3: Pourbaix diagram of a galvannealed steel zinc layer (90% Zn, 10%Fe) in water: At room temperature, atmospheric pressure. Diagram generated with Materialsproject app [14].

### 2.1.2. High-strength steel

High-strength steels (HSS) are steels which contain 0.05% to 0.25% carbon, up to 2.0% manganese and small amounts of other alloying elements such as titanium, vanadium, niobium, etc. The alloying elements strengthen the mechanical properties by acting as second phase nucleation sites and thereby promote grain refinement, which results in higher strength than regular carbon steels. Because HSS contain many spore elements, it is difficult to generate a good Pourbaix diagram for it. We therefore take the Pourbaix diagram of pure iron as a reference (see figure 2.4). If we apply the same
conditions as we did for GA, we can see that at pH 7 and in aerated conditions a passive layer is formed: iron oxide. Under non oxygen conditions, iron hydroxide ions are formed and the iron corrodes. Only if we go the very low potentials the iron is in the immunity region.

![Figure 2.4: Pourbaix diagram of iron in water. At room temperature, atmospheric pressure. Diagram generated with Materialsproject app [14].](image)

In an early stage, corrosion of HSS is faster than for example mild steel. This can be explained by the many fine grains in HSS, which all can be seen as microelectrochemical cells. Due to the occurrence of many grains, there will also be many reactive grain boundaries. All of this combined makes the steel highly electrochemical reactive and prone to fast corrosion. In a later stage however, HSS show better corrosion resistance, due to its fine grains, which promote the formation of a denser (but still porous) passive layer. Furthermore, the reactive grain boundaries increase the dissolution of ferrite around small cathodic cementite particles, which therefore can easily detach. This leaves the substrate with less cathodic sites and therefore less anodic-cathodic couples to start corrosion. In other words, HSS have better corrosion resistance than conventional steels due to their grain size. Other than that, corrosion behaviour is quite similar to conventional steels [15].

### 2.2. Current corrosion protection methods

In order to prevent corrosion, automotive industries generally apply barriers against corrosion. Wax, sealers, plastic covers, and coatings are the most commonly found corrosion protection methods in this industry. Here, the focus will explicitly lie on the corrosion protection methods for the underbody.

**Wax, sealers and hard cover** During manufacturing of the metallic parts of the car, holes are required in the design for certain processes. Due to these holes, it is sometimes very difficult to have an even layer of coating or a coating at all. It is therefore usually chosen to apply wax to these holes, to reject water from contacting the bare metal (see figure 2.5). Of course, this solution is not very effective, but still provides better protection than without. Crevice or other small gaps are usually filled with a silicon based sealer, but of course this does not provide good protection on the long run. In the higher segment cars, a hard plastic cover is applied over the underbody. This basically protects it against stone chipping, splashing water, etc. Unfortunately, this barrier can still be easily bypassed, because the cover is not directly mounted on the coating. There will still be a gap present between the coating and the cover, in which the corrosive media can settle. In the lower segment, this cover is not even provided, leaving the underbody quite exposed.
Coatings are an important corrosion protection method and they cover almost all external metal parts such as the outer body panels or underbody parts. Not only do coatings provide a protective barrier against the environment, they can also give the car its aesthetics in the form of colour and shine. For the underbody, the coating is a build-up of several layers; a metallic-, conversion- and organic coating (see figure 2.5).

Metallic coating  The metallic coating only applies here to GA steel and is the annealed zinc layer discussed earlier in section 2.1. This layer provides protection in two ways: as a physical barrier and as a sacrificial anode. This coating acts as a barrier which separates the substrate from its environment, preventing reactive species from reaching its surface. Furthermore, if the metallic coating is somehow damaged and the substrate is exposed to the environment, the coating will corrode first instead of the substrate. This is due to galvanic coupling; the metallic layer is less noble than the substrate and will act as an anode, sacrificing itself and preventing the corrosion of the substrate. The metallic coating is around 10 microns thick and contains iron in the case of GA steel. Due to the presence of iron, the layer is slightly brittle and porous and can be characterised by cracks (see figure 2.2) [13, 17].

Conversion coating  On top of the metallic coating or substrate, part of the metal surface is converted into a coating with a chemical or electro-chemical process, the so-called conversion layer. It is used to improve corrosion protection and to give better adherence to the coatings that will be applied later on top.

Among the most frequent used conversion coatings in automotive industry are the phosphate conversion coatings. The phosphate layer is an insoluble electrically isolating layer, which gives a small additional corrosion protection. They are made by applying a mild alkaline phosphate bath after HDG which then is followed by a phosphate treatment. The treatment leads to the formation of phosphate crystals which give a rough surface beneficial for adhesion of the subsequent layers. The layer that will be applied on top will flow into the pores creating a key and lock effect [18]. After phosphating, a rinsing process is applied to seal the porous layer and is usually done with a diluted chromic acid rinse. Of course, alternatives are being sought to replace the chrome rinse due to health concerns [19–21].

Electrodeposited layer  On top of the conversion layer an organic electrodeposited (ED) layer is deposited, which is generally an epoxy coating. The primary function of the ED layer is to prevent corrosion by acting as a physical barrier against corrosive media. Furthermore it is used to increase paint adhesion and to smoothen the surface to give it a flat structure. Unfortunately, electrodeposition comes with relatively high cost. To create an ED layer, a metallic part is placed in a bath and connected electrically. By applying a small current, the metallic part becomes a cathode. A small electric field is generated and epoxy particles in the suspension migrate towards the metallic part and are deposited on top of its surface.

Additional organic coatings  Although not applied on the underbody of the car but on the external car body parts, on top of the ED layer subsequent layers can be added see figure 2.6. These layers are generally organic layers and consists of the primer, basecoat and the clearcoat. The primer is added on top to
provide better adhesion between the ED layer and the subsequent layers. They could also contain corrosion pigments to increase corrosion resistance. The basecoat gives the coating system its colour, but has very low corrosion protection properties. Therefore are clearcoat is added, a thick transparent coating which protects the underlying coatings from the environment, scratches and UV-radiation.

![Automotive coating system applied on pretreated metal](image)

**Figure 2.6**: Automotive coating system applied on pretreated metal: Figure reproduced from Hintze-Bruening [22].

### 2.3. Inhibitors

As already mentioned in the previous section, corrosion inhibitors can be implemented in the primer. Basically, corrosion inhibitors are chemicals that retard the corrosion process and have been around for a long time and have proven to be very effective [23]. They protect the metal by, for example, forming a protective layer on top of the metal and thereby blocking processes needed for corrosion. The basic idea is that when the coating is damaged, the corrosion inhibitors leach out of the coating and actively repair the damage. This provides an extra form of corrosion protection which now has not been implemented yet for the car underbody. It is therefore desired to implement corrosion inhibitors into the ED layer or an additional organic layer added on top of the ED layer. Therefore, inhibitors will be discussed here in more details.

Inhibitors can be classified according to their nature and their mechanism (see figure 2.7).

![General inhibitor class division](image)

**Figure 2.7**: General inhibitor class division

**Inhibitor chemical nature**

Inhibitors can be classified in either of the 3 chemical nature groups; inorganic, organic or mixed. The inorganic inhibitors are usually salts and generally work by stifling the anodic, cathodic or both corrosion reactions. Some examples of inorganic inhibitor are silicates, molybdates, tungstates, etc. [23]. The organic inhibitors are of an organic nature and can also stifle the anodic or cathodic corrosion reactions, but are generally acting on both. They usually protect the metal by adhering to the surface and
forming a dense layer which blocks corrosion reactions from occurring. There are several mechanisms in which organic inhibitors adhere to the metal surface. One of those mechanisms is by the donation of a lone pair of electrons to metal atoms, which usually involves the use of heterocyclic compounds or molecules containing O, N or S atoms [24]. Polar groups of the molecule could also bond to either the anodic or cathodic part of the metal. When bonded to the metallic surface, the oleophilic part of the molecule forms a dense layer, which prevents water from wetting the metallic surface and thus preventing corrosion to initiate (see figure 2.10). Here, the protective film is the key to protection, rather than preventing the anodic or cathodic reaction to occur. Some examples of organic inhibitor are amines, urea, 2-mercaptobenzothiazole (MBT), aldehydes, etc [25]. Mixed inhibitors are inhibitors that have both inorganic and organic features. Depending on their chemical build up, they can have a variety of mechanisms. For example, they can initially form an adhering layer just like organic inhibitors. When corrosion occurs, part of their organic chains hydrolyse and release a cathodic inhibitor. That inhibitor further suppresses corrosion. Blin et al. showed this with cerium cinnamate [26]. The cinnamate would form the adhering layer and the cerium would be released when corrosion caused a pH change. This dual effect proved to be highly efficient.

**Inhibitor mechanism**

In most cases, inhibitors are based on one or more of the following mechanisms:

- The inhibitor forms an oxide layer of the base metal which acts as a barrier for corrosion.
- The inhibitor is chemically adsorbed on the metal surface and forms a protective film.
- The inhibitor reacts with the potential corrosive component in the aqueous media forming a complex and thereby effectively lowering or removing the corrosive components.
- The inhibitor acts as a pH buffer.

These mechanisms can be classified according to a group:

**Anodic inhibitors** These inhibitors react with the initially formed corrosion products: the metallic ions in the electrolyte due to dissolution of the metal. A metal oxide film is formed on the anodic metal surface, which protects it and blocks the anodic reaction (see figure 2.8) [27]. It must be noted that the anodic inhibitor concentration must be sufficient, or else some sites will be left uncovered and thus vulnerable. This can result in, or even accelerate, localized corrosion such as pitting [28]. Some examples of anodic inorganic inhibitors are nitrates, molybdates, sodium chromates and phosphates [23, 29].

![Figure 2.8: Mechanism anodic inhibitors: The anodic inhibitors reacts with the metallic ions (Me\(^{n+}\)) which are formed due to the anodic dissolution reaction. They form an insoluble metaloxide film on the anodic sites. The layer hinders further generated Me\(^{n+}\) ions from passing through and thereby stifling the anodic reaction. The hydrolysis of the inhibitors can generate OH\(^-\) ions.](image)

**Cathodic inhibitors** These inhibitors contain metallic ions which form an insoluble layer on top of the cathodic sites. For example, when oxygen is reduced on the cathodic site, OH\(^-\) ions are formed. These will react with the inhibitors to form a hydroxide layer, which is deposited on top of the cathodic sites. This hydroxide layer prevents reductive species, such as oxygen, from diffusing to the cathodic sites, effectively blocking the cathodic reaction (see figure 2.9). Usually, divalent cations are used in these kinds of inhibitors, i.e. zinc and calcium. Cathodic inhibitors can also act as oxygen scavengers, reacting with the dissolved oxygen before it reacts with the metal and thereby hindering the cathodic reaction. Cathodic inhibitors generally do not form a strong insoluble layer and do not bond tightly to the metal...
surface. However, after the critical concentration has been reached, they are no longer concentration-dependant, because they cover the whole surface [23, 29].

**Figure 2.9:** Mechanism cathodic inhibitors: The cathodic inhibitors react with certain corrosion species, such as \( \text{OH}^- \), and form a barrier of insoluble precipitates over the metal, covering it. Thus forming a physical barrier against the environment and hindering the cathodic reaction.

**Mixed inhibitors** Of course, an inhibitor can exhibit both anodic and cathodic inhibition. A mixture of anodic and cathodic inhibitors can also be considered as a mixed inhibitor. These inhibitors do not have a preferential site and will therefore cover the whole surface area (see figure 2.10). Generally, these types of inhibitors will form a film either by physisorption or chemisorption. The first involves bonding to the substrate with weak intermolecular forces such as van der Waal forces. The latter involves forming strong covalent bonds with the substrate. Generally, organic inhibitors tend to be mixed inhibitors.

**Figure 2.10:** Mechanism of mixed inhibitors: The inhibitors has no preferential site and will cover the whole surface area, either by physisorption or chemisorption.

**pH buffering inhibitors** Corrosion can also be inhibited by controlling the pH with pH buffering inhibitors. The buffering action of the inhibitor keeps the pH in a certain range in which corrosion is minimal. For example, under acidic conditions corrosion tends to be accelerated for most metals, whereas at alkaline conditions this largely depends on the metal substrate. Aluminium, for example, tends to corrode at alkaline pH values above 10 due to dissolution of its protecting oxide layer. In contrast, corrosion of steel is generally greatly surprised under alkaline conditions. The pH buffering inhibitors, such as phosphates and borates, are frequently applied as corrosion inhibitors in coolants [30].

**Inhibitor considerations**

The concept of inhibitors seem very straightforward, the application however is generally not. As already mentioned in the beginning of this section, inhibitors can be applied by doping them directly into the primer as a pigment. Unfortunately, this direct doping poses challenges. The inhibitor must match the matrix or else problem arises such as osmotic pressure build-up, delamination, unwanted inhibitor leach out, stability issues, efficiency loss and coating degradation [31, 32]. This means that even if one finds the most effective inhibitor for a certain substrate, if it does not match its designated matrix, it still cannot be used. A less effective inhibitor must then be chosen, which of course is not very desirable. Inhibitor effectiveness itself also depends on many factors, such as type, concentration, substrate, pH, temperature, etc. Inhibitors are highly specific; inhibitor that works very well for a certain corrosion problem, might be useless for another. A change in one of the parameters can have serious consequences for the effectiveness. For example, a slight pH drop might cause an inhibitor to change its conformation to a
less favourable one and therefore a decrease in its performance. Furthermore, besides the above, one should also consider the economics, industrial scalability, environmental impact, etc. The latter, for example, can be a very big issue. In the recent past, chromates have been extensively used due their effectiveness. However, it has been found that despite having superior corrosion protecting abilities, chromates were prone to leaching out and entering the environment. The hexavalent chromium species could damage DNA and eventually cause cancer when frequently exposed to it. [19, 20]. Especially inhaling, during application, causes high risk of lung cancer. The kidneys and liver are also prone to damage when the chromates are ingested. As a result, regulation was set up to minimize the usage of chromates in industry. For example, the EU regulation, REACH, has been formulated and has put the chromates on a list of Substances of Very High Concern (SVHC) [21, 33].

2.4. Smart coatings

The current corrosion prevention methods in the automotive industry provide protection, but they still fail in due time. There will always be a certain degree of permeability when submerged in an aqueous environment. Diffusion or osmosis caused by impurities may occur, which can result in cosmetic corrosion such as filiform corrosion [31]. Also poor curing of the polymer, air entrapment and wrong solvent evaporation may cause a capillary force that attracts moisture. Furthermore, local defects caused by, for example, sudden rupture due to weathering and stone chipping, can cause localised corrosion if the bare metal is exposed. When this concerns a structural element, safety cannot be fully assured.

The addition of inhibitors in the coating can provide a method to actively protect the substrate even after coating failure has occurred. Unfortunately, as already mentioned in the previous section, direct doping of inhibitors can pose problems. To avoid these problems, one could resort to the so-called “smart coatings”; coatings that respond to the environment and behave accordingly, without the need of human interaction. These coatings can contain encapsulated inhibitors that release their content only when necessary. Smart coatings belong to the class of self-healing materials. Here, a brief introduction is given about self-healing materials, to establish the foundation regarding smart coatings.

2.4.1. Self-healing principle

The lifetime of traditional materials rely on improving their overall performance. After a certain time degradation occurs due to accumulating of damages, which lowers their lifetime. Unlike traditional materials, self-healing materials have the ability to autonomously detect and heal (visible or non-visible) damage. This extends their lifetime, gives a potential increase in performance, safety and reliability. These materials have been known to exist during ancient Roman times in the form of self-repairing lime mortar, but they have only received scientific interests until recently. The inspiration for these materials comes from biological systems, which have the ability to heal themselves after being wounded. Recent developments have created materials that can recover a high amount of damage, but to obtain 100% recovery, it is required that the new interface formed has exactly the same properties as the bulk material, which has not been achieved yet. Ideally, the goal is to develop a self-healing material that should fully recover damages without losing its efficiency and therefore have an infinite lifetime (see figure 2.11).
Self-healing materials cover almost all material classes, including metals, polymers, ceramics, etc. The mechanisms involving self-healing can vary among each materials class, but generally two distinct forms of healing can be distinguished; intrinsic healing and extrinsic healing (see figure 2.12).

**Intrinsic healing**

The principle of intrinsic healing lies in the mobility of the molecules in the matrix. When damage has occurred, a softening step needs to be triggered (i.e. heat, light), which leads to a temporary local mobility of the molecules towards the damage. A hardening process is then required by removing the external stimulus, which leads to the restoration of the surface [35] (see figure 2.13).

There are many mechanisms involving the same general approach. An example is the use of a reversible covalent bonding. The polymers involved are based on thermally reversible reactions, particularly the Diels-Alder (DA) reaction to cross-link polymers [36, 37]. Polymers with a diene or dienophile functional group react together and form a network. Upon heating, the retro DA reaction takes place and the monomers can diffuse towards the damaged area. Upon cooling, the DA reaction takes place again and the polymer chains polymerize at the damage area and the material is "healed".

**Extrinsic healing**

The advantage of intrinsic systems is that they are relatively easy to produce and therefore mass production is possible. However, the disadvantage of these systems is that they are not autonomously heal-
ing, which is not desirable especially with minor non-visible damages such as light scratches or blisters. Furthermore, one needs to know the exact location of the damage and apply a stimulus on that specific area or apply it on the whole part if the location is unknown. In the time between noticing a damage and repairing it, corrosion could already have been taken place or could have been further grown. For the underbody of the car, these types of self-healing materials are therefore not really feasible. Corrosion affects the critical structural parts there and adequate healing is mandatory.

**Extrinsic healing**

With extrinsic healing, the matrix cannot heal itself, but requires a self-healing agent i.e. resin, a catalyst or inhibitors, which is usually stored in the matrix by encapsulation. Once damage occurs, the encapsulation breaks or becomes permeable and releases the healing agent that can flow towards the damaged zone. Once arrived, the liquid hardens or reacts with the metal forming a protective layer and restores the damage (see figure 2.14 and 2.16). The extrinsic healing class can be subdivided into the capsule based and vascular self-healing materials:

**Capsule based** The capsule based class uses small containers which are filled with a healing agent. Upon rupture or some sort of stimulus, the agent is released and heals the material in the process (see figure 2.14a). Stimuli can be local pH changes, temperature changes, electromagnetic irradiation, mechanical pressure, humidity, electric or electrochemical potential, ionic strength and dielectric permeability [23, 38].

![Figure 2.14: Schematic extrinsic healing](image)

Several capsule architectures have been developed in the past couple of decades which can differ in size (nano to micro scale), chemical nature (organic or inorganic), shape (plate, sphere, etc.) and structure (layered, porous, etc.). A simple example is the creation of hollow spheres formed by layer-by-layer assembly, which uses a charged particle as its core. Alternate layers of positive and negative polyelectric polymers are deposited on this core, creating a shell. Via an acid treatment the oxide core is removed and a capsule is made (see figure 2.15) [23, 40]. Some other examples are mesoporous silica, aluminum oxide, zirconia, zeolites, etc. [23, 38, 41, 42]. Due to the large variety in capsules and their response mechanisms, it is possible to construct a coating with multiple containers which reacts to a range or specific stimuli, which aids the development of a smart system.
The biggest disadvantage of capsule based extrinsic systems is that once they have healed an area and have exhausted their contents, they cannot heal the same area effectively for the second time. Another problem that might occur is that the capsules can sometimes destabilize the coating to which they were added or cause osmotic blistering [43, 44]. The latter occurs when its content is a salt or substance which has a high solubility and therefore attracts moisture and causes blisters. Stability and solubility should therefore always be checked beforehand. Furthermore, careful considerations should be made when selecting a type of capsule, because it also needs to be matched with the matrix it is dispersed in. For example, silica nanocontainers have very different mechanical properties compared to polymer-based coatings and mixing should therefore be avoided. In this case, polymer based nanocontainers are more suitable [41].

**Vascular based** The vascular class has its origin inspired by nature as it mimics the body vessels in the human body. Microchannels incorporated into the matrix break upon damage or stimulus of the material, releasing the healing agent (see figure 2.16a) [23, 45, 46]. The idea for vascular based materials is the ability to continuously provide the healing agent till full recovery is achieved. Capsule based materials lack continuity and replenishment of healing agent. Besides healing, a vascular network has also the possibility to reinforce the matrix. Pang et al. demonstrated this by filling hollow glass fibre with hardening resin and incorporated this into an epoxy matrix [47]. Specimens with incorporated hollow glass fibres showed good recovery of flexural strength in a 4-point bending test. The downside of vascular based healing materials is that they are quite complex and not really suitable for mass production yet.

![Figure 2.15: Schematic of forming a hollow sphere capsule by the layer-by-layer approach. The core is made out of a negative charged particle. When adding positively charged polyelectric polymers to this particle, a layer is formed. By applying the same step, but with negative charged polyelectric polymers instead, a second layer is added. By repeating these steps, a thicker shell is created layer-by-layer. The core can be removed by a treatment, which leaves the sphere hollow. Figure reproduced from Stankiewicz et al. [41].](image1)

![Figure 2.16: Schematic extrinsic healing: The vascular tubes contain a self-healing agent. Upon damage or stimulus, this agent is released and heals the damaged area. Figure (b) reproduced from Time to heal: The materials that repair themselves [39].](image2)

**2.4.2. Smart coatings for car underbody**

From the basic knowledge about self-healing materials mentioned previously, extrinsic capsule based self-healing materials seem to be the most promising concept to develop a smart coating for the underbody. Due to encapsulation, the inhibitor and matrix are physically separated, thus preventing the
inhibitor-matrix incompatibility. However, the capsule-matrix compatibility still needs to be considered. This is still more preferable, because this still allows the use of the most effective inhibitor, instead of a lesser effective one which matches the matrix.

Furthermore, as already mentioned, controlled release is possible with encapsulation. This prevents unnecessary release, thus allowing a longer lifetime of the coating. Another advantage is that extrinsic self-healing materials is a form of active healing: the materials actively heals its damage and the healing occurs rapidly after damage. The consumer does not need to spot the damage to repair it, nor does it need equipment to do so. This can reduce inspection times, maintenance costs and perhaps improve public image.

Finally, the encapsulation also allows the use of two healing systems: healing by inhibitors and healing by polymer resin. The first heals the metallic substrate, while the latter heals the organic coating (see figure 2.17).

Many examples of using inhibitors as a healing agent in self-healing coatings exist such as Sonawane et al., who loaded benzotriazole in ZnO layer-by-layer nanocontainers [40]. Snihirova et al. reported to load hydroxyapatite microparticles with four different inhibitors to protect its substrate [48]. The reader is referred to the literature for more examples of inhibitor encapsulation and smart coatings [33, 42, 49–51].

![Figure 2.17](image-url)

Figure 2.17: Schematic Illustration of autonomous response of a smart coating to environmental triggers: UV radiation from the sun can trigger polymer healing agents, which can recover the topcoat. The inhibitors are released from their encapsulation due to a water uptake by the coating. Figure reproduced from Cole et al. [51].

2.5. Summary

The underbody of the car, especially the floor and suspensions, are prone to corrosion. During regular use, they can be subjected to up splashing water, de-icing salts and stone chipping. These can damage the galvannealed steel and high strength steel parts.

To protect them against corrosion, current protection methods such as wax, covers and coatings are applied, but they are not sufficient. One could resort to corrosion inhibitors, chemicals that retard the formation of corrosion. These inhibitors should be added to a coating placed on the underbody, but unfortunately this might pose problems due to incompatibility.

Therefore, there is the desire to develop a smart coating that can actively protect the underbody of the car. This coating incorporates extrinsic self-healing with encapsulated corrosion inhibitors. The inhibitors are physically separated from the coating and therefore incompatibility issues with the coating can be avoided. Furthermore, a smart release of inhibitor is possible, which can increase the duration of protection by the coating.

The development of the smart coating will of course take several years and in this present study, only the initial steps will be taken; the search of an effective inhibitor for the car underbody substrates.
Methods & Experimental

In this chapter the experimental methods will be briefly explained. For more in depth information about the techniques, the reader is referred to the literature [52–54]. Next, the experimental procedures are presented.

3.1. Principles of analysis techniques used in this work

3.1.1. Surface analysis

To investigate corrosion products under influence of inhibitors, surface analyse will be used.

Scanning Electron Microscope & Energy-dispersive X-ray spectroscopy

The Scanning Electron Microscope (SEM) and Energy-dispersive X-ray spectroscopy (EDS) allows the user to determine structure morphology and composition of the surface substrate. Some applications are, for example, studies in fractured surface, phase segregation and grain boundary studies. With SEM, a sample surface can be magnified from 10 up to 500,000 times (range from 5 nm to 1 cm).

The principle of SEM imaging lies in the electrons. A concentrated beam shoots electrons at the sample, which interact with the sample and generate electrons with different natures. Those are collected with an appropriate detector and translated into an image. The nature of the emitted electron lies on its collision with the sample (see figure 3.1).

Electrons that have collided inelastically can cause ionisation of the sample material atoms. The collided electrons with lower energy will continue to travel into the sample and ionise other atoms. This cascade effect will generate the so-called secondary electrons, from which signal is used in SEM imaging. Upon relaxation of the atoms, x-rays, photons and Auger-electrons can also be generated. They are
caused by the ejection of an inner shell electron. That electron will be compensated by an electron in a higher orbital dropping down and filling the vacant energy level. This process generates Auger electrons and x-rays. The x-rays can be used to qualitatively and quantitatively determine elements in the sample. The Auger electrons can be used for Auger Electron Spectroscopy (AES), which cannot be used by the SEM due to insufficient vacuum.

The backscatter-electrons are the electrons that have been deflected elastically over large angles with an atom. Heavier atoms scatter the electrons more strongly than light atoms and therefore they will appear lighter on the image. With back-scatter electrons a clear contrast can be made between areas with different chemical composition.

The depth of analysis depends on which emitted electrons are used (see figure 3.2). The high kinetic energy back-scatter electrons can come from relatively deep (typically 1 \( \mu m \) below the surface) from the material. The low-energy secondary electrons can only penetrate up to 50 nm below the surface. The x-rays can easily penetrate the material, but are generated close to a few micrometres from the surface. The Auger electrons can only emanate from only 50 nm from the surface.

EDS is usually used in junction with SEM. When an electron of the primary beam hits a sample atom, part of the kinetic energy is transferred to the sample electrons in the (sub) shells. If an electron receives an energy exceeding its binding energy, that electron will be removed from the shell and leaves the atom ionised. The vacancy that is created will be immediately filled up by an electron from the outer shells. This process generates photons or x-rays. For each element, the emission of x-rays has a characteristic energy, which can be used to determine elemental composition of the sample, qualitatively and quantitatively.

Unfortunately, SEM does come with limitations. The sample must always be solid, conductive, be stable under vacuum conditions and the sample has size limitations. Furthermore, the EDS has difficulties to detect light elements (atomic number < 11). Since ionizing a light atom will be less likely to emit an X-ray, this results in a weaker signal. The sample itself will absorb most of this signal and therefore much of the X-rays detected will be from near the surface of the sample. Sample contamination or coatings used to avoid charging will, as a result, strongly affect the light element analysis.

Figure 3.2: Schematic cross section of the focussed area: The signals emitted come from various parts of the analysing volume: Figure reproduced from C.Kwakernaak [60].
**Fourier Transform Infrared Spectroscopy**

Fourier Transform Infrared Spectroscopy (FTIR) is a powerful tool to investigate the chemical composition and structures of compounds. An infrared beam containing many frequencies is shone on the sample, which will absorb part of the energy. The absorbed IR light induces transitions between the vibrational energy levels of the molecules in the sample, i.e. symmetric stretching, bending, rocking, rotation (see figure 3.3). The reflected beam (with part of the energy absorbed) is detected by a detector and gives an interference pattern. This data is converted with Fourier transformation by the computer into a spectrum, which is basically the molecular “fingerprint” of the sample.

A certain position in the spectrum can correlate to a specific type of bond. For example, an absorption peak at around 1100 can indicate a C=O bond. IR spectra are usually recorded between 4000 cm\(^{-1}\) to 600 cm\(^{-1}\), which can be divided into two approximate regions [61]:

- The functional group region (4000-1000 cm\(^{-1}\))
- The “fingerprint” region (<1000 cm\(^{-1}\))

Two unique molecular structures can give the same peaks for their functional groups, but cannot have the same peaks in their fingerprint region. The intensity of a band is determined by the dipole moment of the bond and the amount of that specific bond present in the sample. With the above mentioned, one can thus identify a material by the position of the absorption bands in the spectrum, the intensity of the band and its shape.

Unfortunately, depending of multiple factors such wavelength, refractive index, angle of incidence, etc. normal FTIR settings are unsuitable for measuring very thin layers, such as monolayers. This problem can be resolved by using grazing angle equipment that increases the angle of incidence (see figure 3.4a). This makes it possible to measure monolayers such as films. Due to the grazing angle equipment, the path of travel of light is increased and it will resolve in better definition of the peaks in the spectrum (see figure 3.4b).

![Figure 3.3: Schematic of main vibrational modes found in silicates: Figure adapted from Aguiar et al. [62].](image-url)
(a) Infrared energy striking a reflective substrate with a thin film on top at a grazing angle of incidence: Due to the large incident angle, the path length through the sample is larger, which increase sensitivity.

(b) FTIR spectrum comparison of a 0.2 mm silicone film on aluminum analyzed at 30° and 75°

Figure 3.4: FTIR with grazing angle equipment: Figure reproduced from T. A. Hoffard [63].
3.1.2. Electrochemical analysis

To investigate inhibition performance and the inhibitor mechanism, electrochemical analysis methods are used.

**Linear Sweep Voltammetry**

When a metal is immersed in an aqueous solution, a generalised reaction for the metal dissolution can be expressed as:

\[ M \rightarrow M^{n+} + ne \]  

(3.1)

Initially, a Helmholtz double layer will be formed, which is a layer of aligned water molecules. This is due to an electric field caused by applying a potential to the metal. The Helmholtz double layer prevents ions from easily passing this layer, thus forming a potential barrier. With this in mind, the rate of metal dissolution can be expressed as an Arrhenius relationship:

\[ k = k_0 \exp \left( -\frac{\Delta G}{RT} \right) \]  

(3.2)

Due to the reaction involving electrons, the kinetics can be expressed by a current density, \( i \):

\[ i_0 = nFk_0 = nFk_0 \exp \left( -\frac{\Delta G}{RT} \right) \]  

(3.3)

In which \( i_0 \) is the exchange current density, the current flowing in both direction when the electrode is in equilibrium. By applying an overpotential to noble or less noble values, to overcome the Helmholtz double layer, the activation energy is changed and can be expressed as:

\[ i_{\text{anode}} = i_{\text{cathode}} = i_0 \exp \left( \frac{azF\eta}{RT} \right) \]  

(3.4)

This equation is known as the Tafel equation. Generally, this equations is expressed in the form:

\[ \eta = a + b \log i \]  

(3.5)

, with \( a = -\frac{2.303RT}{nF} \log i_0 \). The equation can be plotted in a so-called Evans diagram. In figure 3.5, the blue lines are the Tafel plots for the iron reaction at the anodic sites. The black lines represent hydrogen Tafel plots at the cathodic sites. When the anode and cathode are coupled, i.e. by an electrolyte, the two central branches will form a new Tafel plot. This is shown by the red lines and represents the Tafel plot for corrosion. The intersection of the two branches, gives the corrosion current density: \( i_{\text{corr}} \).

This parameter tells us how fast our system is corroding; it can be expressed in a corrosion rate in mm/year:

\[ r = \frac{a \cdot i_{\text{corr}}}{n \cdot F \cdot D} \]  

(3.6)

with \( a \) the atomic mass [g/mol], \( n \) the number of electrons exchanged in the reaction, \( F \) the Faraday constant [96.500 C/mol], \( i \) the current density [A/m²] and \( D \) the density [g/m³].
By sweeping an external potential linearly with Linear Sweep Voltammetry (LSV), one obtains a polarization curve (see figure 3.7). From this curve, the tangents of both the anodic and cathodic tail of the curve at ±250 mV from \( E_{corr} \) are taken (see figure 3.6). The intersection of the tangents gives \( i_{corr} \). Notice that the red curve from figure 3.5 is essentially the polarisation curve close to the free corrosion potential, \( E_{corr} \).

Of course, figure 3.6 shows an ideal example. Real measurements often give non-ideal curves. For example, the anodic tail can be very horizontal, implying a very active surface. In this case, measurements at a lower concentration of the corrosive medium is required. Sometimes it is just not possible to take the tangent in the ±250 mV range, even by lowering the concentration. Then, the rule of thumb is applied: take the most linear part and try to still be in the 250 mV range. Smaller values are allowed, but are not preferred (see figure 3.7). The ±250 mV is just a guideline and no hard rule. This is to prevent taking Tafel lines that are too close to the equilibrium, in which the Tafel equations are not valid.

For the cathodic tail, the bending of the curve can occur very close to the \( E_{corr} \). To still obtain the cathodic tafel tangent, also here the most linear part is taken. This is the area where generally oxygen diffusion is limited.
3.1. Principles of analysis techniques used in this work

Figure 3.6: Schematic illustration of the Tafel extrapolation method: By taking the tangent (dashed lines) of both the cathodic and anodic tails at ± 250 mV from $E_{\text{corr}}$ (blue lines), the intersection of the tangents will give $i_{\text{corr}}$. Figure reproduced from Zhang et al. [56].

Furthermore, with LSV it is possible to indicate if an applied inhibitor has a cathodic, anodic or mixed nature by measuring the shift relatively to $E_{\text{corr}}$ and $i_{\text{corr}}$. An anodic inhibitor would shift the curve to more noble values and lower current density, whereas an cathodic inhibitor would shift the curves to more negative values and lower current density. With a mixed inhibitor, both anodic and cathodic tails are affected. The shift in potential will be absent, but there will be a decrease in corrosion current density (see figure 3.8). The lower current density caused by an inhibitor can be compared with the blank expressed in an efficiency, the inhibitor efficiency:

$$\eta = \frac{i_{\text{corr}} - i_{\text{inhib}}}{i_{\text{corr}}} \times 100\%$$ (3.7)
Methods & Experimental

Figure 3.8: Schematic tafel plots for different types of inhibitors: (a) A cathodic inhibitor, which shifts $E_R$ to more negative potentials and $i_C$ to lower values. (b) An anodic inhibitor, which shifts $E_R$ to more positive potentials and $i_C$ to lower values. A mixed inhibitor, which shifts only $i_C$ to lower values. Figure reproduced from Marcus et al. [52].

Electrochemical Impedance Spectroscopy

Each material, as well as corrosion process, has its own resistance to current flow. Basically, one could see a corrosion process as a sum of complex electrical circuits. By measuring the responds to an applied current, one could extract information about the material and the processes involved. Electrochemical Impedance Spectroscopy (EIS) has its principle based on this. The data provided by EIS is rich in data, which makes it very versatile and allows the user to characterize the kinetics of certain processes, resistances and capacitances, which simple voltammetric techniques cannot provide. In most electrochemical techniques a DC potential is used, while in contrast, EIS uses an AC potential expressed as:

$$E_t = E_0 \sin(\omega t)$$  \hspace{1cm} (3.8)

By slightly perturbing the sample with a small AC potential, a pseudo-linear current response is provoked:

$$I_t = I_0 \sin(\omega t + \phi)$$  \hspace{1cm} (3.9)

In analogy with Ohm’s law, the impedance can be defined as:

$$Z = \frac{E_t}{I_t} = \frac{E_0 \sin(\omega t)}{I_0 \sin(\omega t + \phi)} = Z_0 \frac{\sin(\omega t)}{\sin(\omega t + \phi)}$$  \hspace{1cm} (3.10)

By plotting $E$ versus $I$, one would get a Lissajous figure, which is quite difficult to interpret. By using Euler’s formula for complex numbers, the above equation can be represented as:

$$Z(\omega) = \frac{E}{I} = Z_0 \exp(j\phi) = Z_0(\cos \phi + j\sin \phi)$$  \hspace{1cm} (3.11)
The complex impedance data can be graphically represented in two ways: a complex plane plot or a Bode plot (see figure 3.9). With the complex plane plot, frequently called "Nyquist plot", the impedance is represented as a vector of absolute length $|Z|$ in a complex plane. The Bode plot on the other hand, graphically present the EIS data in the log frequency versus the absolute impedance or the phase shift. The Bode plot allows better observation of small changes in time compared to the Nyquist plot. Especially in coatings, where water permeability occurs, Bode plots can be very useful (see figure 3.10). In literature, both plots are generally used, especially when the data needs to be fitted to a model.

A term frequently used is the time constant, $\tau$, with $\tau = RC$ and $\omega = \frac{1}{\sqrt{RC}}$. Generally, this is the maximum which can be found in the Nyquist plot. In the Bode plot this is the phase angle deflection point. If the time constant and capacitance is known, the resistance can be calculated. This can be used to calculate inhibitor efficiencies by the following formula [58]:

$$\eta = \frac{R_{inhib} - R_{corr}}{R_{corr}} \times 100\%$$

(3.12)

As already was mentioned, real life systems involve very complex process that can be represented by complex electric circuits. The circuits are composed of individual elements, which represent the differ-
ent impedance responses. The elements are summarised in Table 3.1. By combining these elements, one can obtain the equivalence circuit, which can explain the possible corrosion mechanism. Each element in the table has a certain impedance and Ohm’s law applies when combining these elements. For example, let us take the circuit from Figure 3.9a, which can be seen as a series of resistances ($R_s + R_{R+C}$). The resistance $R_{R+C}$ can be seen as a resistance $R$ and a capacitance $C$ in parallel. By applying Ohm’s law for series ($R_{\text{total}} = R_1 + R_2 + ... + R_n$) and parallel circuits ($R_{\text{total}} = \frac{1}{\frac{1}{R_1} + \frac{1}{R_2} + ... + \frac{1}{R_n}}$), the circuit given gives an impedance of $R_s + \frac{1}{\frac{1}{R} + j\omega C}$. In the complex plane this gives a semi-circle.

Table 3.1: Common electrical elements used in EIS

<table>
<thead>
<tr>
<th>Equivalent element</th>
<th>Impedance</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>R</td>
<td>$R$</td>
<td>Resistance, generally represents a corrosive medium.</td>
</tr>
<tr>
<td>C</td>
<td>$\frac{1}{j\omega}$</td>
<td>Capacitance, generally represents a coating, electric double layer capacitance, etc.</td>
</tr>
<tr>
<td>L</td>
<td>$j\omega C$</td>
<td>Inductor, is uncommon in corrosion. If it occurs, then it is perhaps errors, fouling, instability, etc.</td>
</tr>
<tr>
<td>W</td>
<td>$\frac{1}{\sqrt{\frac{R}{j\omega}}}$</td>
<td>Infinite Warburg impedance, is impedance caused by diffusion if the layer has infinite thickness.</td>
</tr>
<tr>
<td>O</td>
<td>$\frac{\tanh(\frac{R/\sqrt{j\omega}}{\sqrt{\frac{R}{j\omega}}})}{\sqrt{\frac{R}{j\omega}}}$</td>
<td>Finite Warburg impedance, is impedance caused by diffusion if the layer has finite thickness.</td>
</tr>
<tr>
<td>Q</td>
<td>$\frac{1}{\sqrt{\frac{R}{j\omega}}}$</td>
<td>Constant phase element, is used to model an imperfect double layer capacitor. Has no physical meaning, but is used to model non-ideality.</td>
</tr>
</tbody>
</table>

Impedance data can be very complex, it can contain loopings, multiple semi-circles, inductive loops, which can be related to different processes such as:
- Mass transfer
- Kinetic effects
- Adsorption
- Hydrogen evolution
- Dispersion

Due to all these factors, it is sometimes not clear what actually happens. It therefore helps to resort to other techniques and compare the data. It should be noted that modelling of circuits is generally done by software provided with the equipment. This software is able to perfectly fit an equivalence circuit to any plot by adding a substantial amount of elements to the circuit. Of course, for the physical interpretation this is meaningless. To make things more complicated, two different circuits can also have the same impedance plot (see Figure 3.11). When interpreting impedance data, a rule of thumb should be applied: add the least amount of elements required and try if possible to confirm the impedance data with other electrochemical techniques. Furthermore, it is also possible to vary certain physical elements, to see if it affects the model likewise.

Figure 3.11: Two equivalent circuits giving the same impedance plot. Both (a) and (b) give one semicircle on complex plane plot and are characterized by one time constant. Furthermore, (a) is a Randles circuit and has a physical meaning, while (b) does not have one. Figure reproduced from Laisa et al. [53].
3.2. Experimental

3.2.1. Materials

Corrosion studies were done on bare steel plates of GA steel and HSS. They were cut into dimensions of 30 × 30 mm and had a thickness of 1.4 mm (GA steel)/3.4 mm (HSS). The samples were degreased with ethanol in an ultrasonic bath for 5 minutes (Branson 3510).

Reference and inhibitor solutions

A reference solution was prepared by dissolving sodium chloride in demiwater (0.05 M or 2.922 g/L). The inhibitors that were used in this study are listed in table 3.2. Inhibitor solutions were prepared by dissolving the required amount of inhibitor (see table 4.6) and sodium chloride (0.05 M or 2.922 g/L) in demiwater.

Table 3.2: List of inhibitors used in this study

<table>
<thead>
<tr>
<th>Name</th>
<th>Compound</th>
<th>CAS Number</th>
<th>Additional info.</th>
</tr>
</thead>
<tbody>
<tr>
<td>238538 Aldrich</td>
<td>Ce(NO₃)₃ · 6H₂O</td>
<td>10294-41-4</td>
<td>-</td>
</tr>
<tr>
<td>793582 Fluka</td>
<td>KI</td>
<td>7681-11-0</td>
<td>-</td>
</tr>
<tr>
<td>63720 Fluka</td>
<td>2-Mercaptobenzothiazole</td>
<td>149-30-4</td>
<td>-</td>
</tr>
<tr>
<td>M1003 Fluka</td>
<td>Na₂MoO₄ · 2H₂O</td>
<td>10102-40-6</td>
<td>-</td>
</tr>
<tr>
<td>307815 Aldrich</td>
<td>Na₂SiO₃</td>
<td>6834-92-0</td>
<td>SiO₂ : Na₂O ratio = 0.9</td>
</tr>
<tr>
<td>T2629 Honeywell</td>
<td>Na₂WO₄ · 2H₂O</td>
<td>10213-10-2</td>
<td>-</td>
</tr>
<tr>
<td>14023 Sigma-Aldrich</td>
<td>TiOSO₄ · xH₂O</td>
<td>13825-74-6</td>
<td>-</td>
</tr>
</tbody>
</table>

3.2.2. Electrochemical studies

Standard 3-electrode electrochemical cells were used in junction with a graphite counter electrode (CE) and a saturated Calomel electrode (SCE) as the reference electrode (see figure 3.12). The steel samples were used as the working electrode (WE). The volume of the electrolyte was around 80 ml. The surface area exposed to the electrolyte was around 2.688 cm². A potentiostat (Solartron 1287) with software from Scribner Associate was used to measure and view the data, respectively, CorrWare V1 and Corview V3. Electrochemical experiments were always done in trifold to confirm reproducibility.

Figure 3.12: Schematic cell set-up: The cell contains 3 electrodes which are connected electrically with the potentiostat; the counter electrode (CE), the reference electrode (SCE) and the working electrode (WE).

LSV

For the OCP measurements, the samples were immersed for 30 minutes and data was collected during that time. LSV data was collected directly after OCP measurements at a scan rate of 1 mV/s⁻¹. Scans were made by sweeping the potential starting from -400 mV vs. OCP to +400 mV vs OCP. Additional scans were made to identify if an inhibitor is anodic/cathodic/mixed, by applying a sweep from ±50 mV vs. OCP to ±400 mV vs OCP.
EIS
Impedance measurement were performed with the same potentiostat and a frequency response analyser equipped with a multiplexer. Electrochemical tests were performed in the same cell set-up as the LSV measurements. A low frequency of 10 mHz and a high frequency of 100 kHz were used. A sinusoidal perturbation of 10 mV amplitude was used as excitation signal.

3.2.3. Inhibition performance in time study
The cutting edges of the GA steel sample were covered with double layer of masking polymer (Turco Form Mask 537-42HT), to avoid galvanic coupling during immersion. The substrates were immersed in inhibitor solution for 8 weeks (for concentrations see figures 4.10 and 4.11). After immersion, the samples were left to dry naturally and pictures were made afterwards.

3.2.4. Surface analysis
SEM & EDS
Samples were made electrically conductive by physical vapour deposition (JEOL, JFC-1300) with gold. Conducting tape was also placed near the edges of the sample to further suppress noise. Magnification varied for each sample.
SEM images and EDS analysis (JEOL, JSM 6480LA) were made with an accelerating voltage of 15 kV and a working distance of 10 mm. An EDX detector of JEOL EX-94300 was used. Multiple areas on the same substrate were analysed to obtain reproducibility.

FTIR
The cutting edges and one side of each sample were covered with double layer of masking polymer (Turco Form Mask 537-42HT), to reduce localised corrosion during immersion and promote uniform corrosion. GA steel samples were prior to masking with polymer rinsed in NaOH solution (pH=10.8) at 40 °C for 5 minutes. This was to remove aluminium, which remains on the surface after HDG process.
After sample immersion, samples were left to dry vertically in a desiccator.
A FTIR spectrometer (Nicolet 6700) equipped with the Smart SAGA accessory was used to obtain grazing angle spectra. Clean (non-immersed) samples were used for the background measurement. Data was collected with a resolution of 8 cm⁻¹ averaged over 128 scans. The recording spectra had a range starting from 4000 to 650 cm⁻¹. The average beam size was around 500 μm in diameter. Experiments were done in trifold to confirm reproducibility.
Screening of corrosion inhibitors

For the development of a smart coating, an appropriate inhibitor must be found first. This chapter will report the process of the corrosion inhibitor screening, which includes a review of the inhibitors found in literature, a preselection based on the literature review and an electrochemical evaluation of the inhibitor efficiency.

4.1. General corrosion mechanisms substrates

Before discussing the inhibitor screening, a brief summary about the corrosion mechanisms is given per substrate to give a better understanding of what needs to be inhibited.

4.1.1. Galvannealed steel

The galvannealed layer consists of roughly 90% zinc and 10% iron. Due to the large quantity in zinc, the corrosion behaviour is somewhat similar to pure zinc [64]. When exposed to a corrosive medium in absence of halides, the zinc will act as a sacrificial anode, preventing the iron substrate from corroding [17]. On the zinc surface the following half reaction takes place:

\[ \text{Zn} \rightarrow \text{Zn}^{2+} + 2e^- \quad \text{at the anodic sites} \quad (4.1) \]

\[ \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} + 2e^- \rightarrow 2\text{OH}^- \quad \text{at the cathodic sites} \quad (4.2) \]

Together with the above reactions this forms the typical white rust layer which consists of zinc hydroxide or zinc oxide on the anodic sites:

\[ \text{Zn}(s) + \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Zn(OH)}_2 \rightleftharpoons \text{ZnO} + \text{H}_2\text{O} \quad (4.3) \]

The layer protects the underlying zinc from further dissolution. However, when chlorides are in the medium, they will break down the protective passive layer and initiate pitting [65]. Several mechanisms can occur, one of them is based on the formation of simonkolleite:

\[ 5\text{ZnO}(s) + 2\text{Cl}^- (aq) + 6\text{H}_2\text{O} \rightarrow \text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}(s) + 2\text{OH}^- \quad (4.4) \]

, which is porous, insoluble and unstable [66]. Due to its porosity, zinc ions and sodium ions are able to diffuse through the simonkolleite layer towards the cathodic sites, allowing zinc dissolution to continue. When the pits reach the underlying metal, pitting of the substrate starts. In generally, zinc is prone to pitting corrosion in halide solutions [57]. Galvannealed steel also exhibits this behaviour, albeit more severe [64]. This is due to surface cracks found frequently on the GA steel zinc layer, which act as preferential sites for pitting [17]. In those cracks, a preferential dissolution of the zinc-rich phases occur.
4.1.2. **High-strength steel**

When high-strength steel corrodes, generally uniform and localised corrosion will occur. The following reactions occur for uniform corrosion:

\[ 2Fe \rightarrow 4e^- + 2Fe^{2+} \text{ at the anodic sites} \]  \hspace{1cm} (4.5)

\[ 4e^- + O_2 + 2H_2O \rightarrow 4OH^- \text{ at the cathodic sites} \]  \hspace{1cm} (4.6)

The above reactions together can result in the formation of iron hydroxide, \( Fe(OH)_2 \). In addition, the Fe(II) from reaction 4.5 can further oxidize if there is sufficient oxygen:

\[ 4Fe^{2+} + O_2 \rightarrow 4Fe^{3+} + 2O^{2-} \]  \hspace{1cm} (4.7)

Depending on the available water and oxygen, iron oxides or hydroxides can be formed [68]:

\[ Fe^{2+} + 2H_2O \rightarrow Fe(OH)_2 + 2H^+ \]

\[ Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+ \]

\[ Fe(OH)_2 \rightarrow FeO + H_2O \]

\[ Fe(OH)_3 \rightarrow FeO(OH) + H_2O \]

\[ 2FeO(OH) \rightarrow Fe_2O_3 + H_2O \]  \hspace{1cm} (4.8)

Two porous corrosion layers usually exist; the more compact inner layer and the less dense outer layer [15]. The fine structure of HSS allows pegging of the inner rust layer, resulting in better adhesion to that layer, which allows the formation of stable scales. HSS therefore exhibits, for example, better corrosion resistance than mild steel, which has a similar corrosion mechanism [69].

When HSS is exposed to a medium containing chlorides, pitting can occur. The chlorides can break down the porous passive layer and initiate pitting. Another possible mechanism is the dissolution of inclusions such as manganese sulphides. These are covered by a weak passive layer, which is attacked faster by chloride ions than the surrounding matrix. This will leave a hole which is an ideal environment for the accumulation of chlorides and the initiation of pitting [70]. Inclusions can also be nobler than the surrounding metal matrix, which causes the inclusion to behave cathodically. The metal matrix surrounding the inclusion will dissolve, which can cause the inclusion to be released from its matrix. This will leave a pit which can propagate.

4.2. **Literature review of corrosion inhibitors for GA steel and HSS**

In literature, inhibitor studies for galvannealed steel and high-strength steel are quite uncommon. On the other hand, galvanized-, carbon- and mild steel are mentioned much more frequently. Even though these metals differ in composition with the substrates in this report, the corrosion mechanisms are roughly the same as mentioned in 4.1. Therefore an assumption was made that steels with a zinc coating (or pure zinc) and forms of mild steel could model inhibition for, respectively, galvannealed steel and high-strength steel. This assumption will provide a good basis to initiate the literature research. The inhibitors will be exposed to extensive testing nevertheless.

There is a substantial amount of information available about corrosion inhibitors in literature. However, general trends can be distinguished still. The inhibitors can be divided in groups to one’s liking, for example, based on inhibitor nature, mechanism, etc. Here, it is chosen to base the division on the chemical composition: oxyanions, organic, miscellaneous and mixtures of inhibitors (see figure 4.1). Each of these groups will be briefly discussed and some of their inhibitors are presented.
4.2. Literature review of corrosion inhibitors for GA steel and HSS

Corrosion inhibitors in literature

- **Oxyanion**
  - Molybdates
  - Nitrates
  - Phosphates
  - Silicates
  - Tungstates

- **Organic**
  - Natural occurring inhibitors
  - Benzazole derivate

- **Miscellaneous**
  - Metal cations
  - Rare earth metals

- **Mixtures of inhibitors**
  - Organic-inorganic mixtures
  - Rare earth metal mixtures

Figure 4.1: Schematic of the inhibitor groups which can be found in literature classified according to their chemical composition

Oxyanion inhibitors
The oxyanions are based on anions which have $A_nO_2^{2-}$ as their common formula, such as nitrates, phosphates, metal oxides, etc. The inhibition mechanism depends on the oxyanions that is being used, as the protection mechanisms can be diverse. Example mechanisms are the creation of a protecting film [71], pH buffering [30], etc.

Oxyanions have a long history of use in corrosion protection. Chromates for example, have been used extensively before it was known that they pose serious environmental issues. Noteworthy inhibitors in this group are:

**Molybdates** The molybdates are generally anodic inhibitors which adhere themselves to the porous hydroxide layer of steel, after which they act as a cation-selective barrier; only certain cations can pass through the barrier, thus preventing corrosive chloride ions from reaching the substrate [72–74]. These inhibitors can also be found in pits on the surface. The molybdate forms molybdocloride in the pits, which may hydrolyse to a molybdate-stabilized oxide film covering the pit. This relaxes the pitting conditions and therefore slows down the growth of the pits. Molybdates have also shown good synergism with many other compounds by combing them through i.e. mixing, synthesis [75]. For example, Zhou et al. showed improved corrosion inhibition on mild steel with a molybdate nitrate mixture compared to pure molybdate[76].

**Nitrites** Nitrites have been frequently investigated, especially in steel reinforced concrete where more alkaline conditions persists. These type of inhibitors are generally anodic inhibitors. They show a high protection efficiency against localised corrosion (i.e. pitting) and only require a low concentration of the salt [77]. Nitrates react with iron hydroxide derived from the corroding substrate to form an iron oxide film, which forms a protecting layer around the active sites of steel [78]. Unfortunately, when high corrosion activity occurs (i.e. pits on propagation state), the inhibitor loses its efficiency. Corrosion acceleration can even occur due to local acidification of the solution as was observed by Zhou et al. [76].

**Phosphates** Phosphates have been extensively researched as well as applied. The zinc phosphate layer as a conversion layer discussed in section 2.2, is an example of its large scale application. These inhibitors can be either anodic, cathodic or mixed, depending of the conditions or type of phosphate [79, 80]. When applied, they will form an insoluble insulating layer which protects the base material. Commercial phosphate inhibitors are widely available and are generally a mixture of multiple pigments. Zin et al., for example, combined one of these commercial pigments to tests if it was possible to obtain synergism. The mixture contained phosphate, molybdate and calcium exchange silica. When applied, the phosphates would precipitate when they came in contact with calcium ions. The mixture gave significantly better corrosion resistance than using the pigments standalone [80].

**Silicates** Silicates, more commonly known as glasses, have been frequently reported as inhibitors for mainly steel [81–84]. They do not prevent the onset of corrosion, instead, they form a double layer of a conglomerate of silicate-metal and silica-gel after corrosion has occurred. Silicates form this double layer by firstly depositing an initial layer on top of the corrosion products. As time progresses, the second layer is deposited on top of the initial layer. The layers act as a barrier against corrosive species, preventing further corrosion.
Beside their individual usage, silicates can also work synergistically: an example is demonstrated by Mohammadi et al. They combined Na₂SiO₃·5H₂O with rare earth metals, which formed a protective film of rare earth oxide/hydroxide and silicon oxide on carbon steel [85].

**Tungstates** The reports of sodium tungstate as a green inhibitor can be often found due to their low toxicity. This makes them very attracted in the search of more environmental friendly corrosion protection techniques. Tungstates generally form a strong insoluble layer by reacting with the iron oxides originating from the steel substrate after corrosion has taken place [86, 87].

**Organic inhibitors** Many organic inhibitors reviewed in literature are based on aromatic compounds, containing an O, N or S atom. Those molecules generally have lone pairs which can form bonds with the metallic surface, due their vacant d-orbitals. As a result, these molecules adhere to either the anodic, cathodic or both sites and form a passive film. These organic can adsorb to the substrate either by physisorption or chemisorption and this adsorption is largely dependent on pH, which controls the degree of adsorption [88–90]. For example, oleic imidazoline (IM) [91] was synthesised by Liu et al. This inhibitor adhered to the substrate surface and could be tailored by varying the length of the stearic chain. Liu concluded that longer chains up to n=18 provided excellent inhibition due to the self-assembly of these molecules which forms a dense layer (see figure 4.2).

Organic inhibitors have attracted research due to their inherent stability and their cost effectiveness. As an example, cheap old expired drugs have even been reported to be used, such as paracetamol, which can achieve 85% efficiency on carbon steel under mild acidic conditions. As a disclaimer however, it is provided that not every drug is suitable. A common example is that of aspirin, which can hydrolyse in a corrosive aqueous solution into salicylic acid and acetic acid. Those acids can accelerate corrosion [92, 93]. However, it must be noted that organic inhibitors are not always inexpensive. Generally, more aromatic rings and O, N and S atoms provide better adherence, thus better corrosion protection, but also increase the price, due to increasing difficulties in synthetization.

![Chemical structure of imidazole molecule](image1)

![Structure of stearic imidazoline](image2)

![Adsorption modeling of IM on the surface of Fe](image3)

*Figure 4.2: Schematic of the layer formation of imidazole (IM): Figures reproduced from Liu et al. [91]*

Due to extensive research based on organic inhibitors, there is a substantial list and the reader is referred to the literature reviews [88, 94].

Two frequently studied groups belonging to the organic inhibitors are:

**Natural occurring inhibitors** These inhibitors are extracted from i.e. plants, animal proteins and can contain heterocyclic constituents such as alkaloids, flavonoids etc. Caffeine, for example, has been reported to give up to 90% inhibition when applied to mild steel [95]. Other examples are: inhibitors made from extracts of mango peels, aloe leaves, rosemary, ginger, etc. [88, 96]. To this date, many plant extracts have not been explored yet for their corrosion inhibition capabilities and research is still going on. Al-Otaibi et al. extracted alcohol from indigenous plants from Saudi Arabia, which could obtain up to 91% of inhibition efficiency when applied to mild steel [97]. Patel et al. even reported an efficiency of 98% with their plant extracts [98]. Although many of these extracts are being investigated and high efficiencies have been achieved, it is not yet fully understood which components of
the extracts give the inhibition. In a lesser extent, animal proteins (i.e. by-products of meat and milk) have also been reported as an anti-corrosion agent to retard i.e. acid corrosion [25].

**Benzazole derivates** These molecules are aromatic organic compounds which differ from each other by varying certain functional groups [94]. They can have varying applications depending in which industry they are applied; one of the applications is as a corrosion inhibitor. A good example is 2-mercaptobenzothiazole (MBT) (see figure 4.3a). This benzazole can be found in many papers which have observed its effective corrosion inhibition. It has been applied on many different substrates, such as steel, aluminium and copper [99, 100]. On galvanized steel, MBT adheres on zinc as well as iron by forming metal complexes with their exocyclic sulphur and nitrogen bonds. Despite their effectiveness, stability issues have been reported, such as photodegradation and instability [101]. Furthermore, there is still discussion ongoing about the toxicity of this inhibitor, as there are plans to place the substance on the list of hazardous compounds that needs to be restricted [102].

A similar molecule, benzotriazole (see figure 4.3a), has also been frequently studied as a corrosion inhibitor for galvanized steel. This molecule competes with chloride ions and forms with Zn\(^{2+}\) a passive layer, preventing corrosion reactions from occurring. Unfortunately, this molecule also has been reported with stability issues such as photodegradation [103].

![Chemical structures of benzazole derivates commonly studied as corrosion inhibitors](image)

Figure 4.3: Chemical structures of benzazole derivates commonly studied as corrosion inhibitors

**Miscellaneous inhibitors**

Metals in their salt form can be also exploited as corrosion inhibitors. Cobalt and nickel ions, for example, have been reported to incorporate themselves in the passive film of zinc (zinc oxide). There, the cobalt and nickel ions can form, respectively, elemental cobalt and nickel by gaining electrons. These ions compete with oxygen for electrons which hinders the cathodic reaction and thus inhibits corrosion. This mechanisms is referred as an electron trap, because the electrons cannot escape from the surface and are trapped in the film [104].

The passive film of titanium is known for its excellent protecting properties and therefore it has been tried to apply this as an inhibitor [105, 106]. Yang et al. have developed a self-healing polymer with oxotitanium sulphate (TiOSO\(_4\)). When the coating was immersed in water, the inhibitor would leach out and dissociate into Ti\(^{2+}\), which is very unstable. These titanium ions would precipitates as TiO, forming a strong barrier against corrosion [107]. Rare earth salts generally are cathodic inhibitors as they generate a protective (hydr)oxide layer on the cathodic sites, blocking oxygen diffusion. Rare earth inhibitors do not prevent the onset of corrosion [108]. They operate at alkaline pH levels, which occurs locally at the cathodic sites when corrosion already has occurred. The rare earth salts have been of interest due to the fact that they are considered environmentally friendly, relatively cheap and they have been proven to be effective at low concentrations.

Many reports have especially been based on cerium salts, such as cerium nitrates and cerium chlorides [109, 110]. Due to oxidation on the cathodic sites:

\[
\frac{1}{2} O_2 + H_2O + 2e^- \rightarrow 2OH^- \quad (4.9)
\]
In a local alkaline environment is created (pH = 8.3). Cerium ions will precipitate and form a protective cerium hydroxide film on the cathodic sites:

\[
Ce^{3+} + 3OH^- \rightarrow Ce(OH)_3
\]  

Furthermore, Ce\(^{3+}\) can also oxidize to Ce\(^{4+}\) and react with hydroxide:

\[
Ce^{4+} + 4OH^- \rightarrow Ce(OH)_4
\]

This will form insoluble cerium hydroxide that has a yellow pale colour, which is also deposited on the cathodic sites [111, 112]. The inhibition by cerium is generally promising, but they seem to be mostly effective at short treatment times, which is not desirable for long time protection in the automotive industry. Besides cerium, other rare earth metals have also been explored, such as lanthanum, yttrium and strontium [112]. It must be noticed that scandium, also belonging to this group, has not yet been reported in literature as an inhibitor. The reason might be due to the difficult isolation of the metal from ores, which result in limited availability and therefore very high costs compared to other rare earth metals [113].

**Mixtures of inhibitors**

By combining inhibitors, one could try to achieve synergism in inhibition; two or more inhibitors that work better together than each individually [114, 115]. One could think of mixing anodic and cathodic inhibitors to obtain mixed inhibition. Or one could synthesize a mixed inhibitor by combining a cathodic metal ion with an organic anodic molecule. The combination of different mechanisms is also an option. For example, one could combine an inhibitor that forms a layer on top of the active sites and an inhibitor that is a pH buffer. Combing inhibitors is straightforward, however the screening of efficient combination of inhibitors is not. Many combinations in terms of type of inhibitors and concentrations to be used are possible, which makes research tedious.

In literature many combinations of inhibitors can be found and certain trends can be distinguished. A topic that draws considerable attention right now, is the combination of organic- and inorganic inhibitors. Tawfik et al. created an anionic surfactant by esterifying phosphate groups with fatty alcohols. The phosphate groups were negatively charged and were attracted to the anodic sites of the steel substrate (physical adsorption). The donor-acceptor π-electrons from the P and O atoms provided chemical adsorption. The long chains of the inhibitor were aliphatic, rejecting water from the metallic surface. The combination of multiple mechanisms provided an inhibition efficiency up to 94.4% on carbon steel [116]. Appa Roa et al. reported to combine three inhibitors that worked synergistically on carbon steel; NN-bis(phosphonomethyl) glycine (BPMG), zinc phosphate and tungstate. The BPMG would form complexes with the zinc ions and precipitate on the substrate, after which it polymerizes and forms a dense layer. The zinc ions can also form zinc hydroxide, which precipitates on the cathodic sites. The tungstate would react with the Fe from the substrate and form another insoluble layer [117]. Rare earth metals synthesized with organocarboxylates with multiple functional groups, also seem very promising [118]. The idea is that the organic part (anodic/mixed inhibition) forms an intermetallic complex with the substrate, forming the initial protecting layer (see figure 4.4). When the pH locally increases due to reduction of oxygen, the rare earth metal (cathodic inhibition) bonded with the organic part hydrolyses. The bond breaks and the rare earth metal is released in solution. Precipitation is followed and a hydroxide layer is formed, due to the exceed of the solubility limit. These two layers work synergistically and result in a very efficient protection mechanism. Blin et al. yielded excellent results with this concept on mild steel. They tested multiple rare earth metals, however lanthanum based ones combined with hydroxide substituted cinnamate prove to be the most efficient, up to 91% [26, 119].
From the above inhibitor literature study an initial screening was made based on the following criteria:

- **The applied substrate** The inhibitor should have been tested on a zinc based substrate, mild steel, HSLA steel or carbon steel. This would allow a better comparison with the substrates used in this report.

- **Mechanism** It is tried to select a variety of inhibitors with different mechanisms. This allows possible synergism, which can be used later.

- **Inhibitor nature** The list should contain a balanced mix of cathodic/anodic/mixed inhibitors. This allows a broader selection window later on.

- **Frequency found in literature** If the inhibitor is frequently mentioned in literature, this usually means it is effective and researched well, which allows better referencing.

Due to the fact that this is the initial screening, the criteria were not applied strictly. If an inhibitor, for example, has a very unique mechanism, but was not frequently reported in literature, it could still have been added to the list. This would narrow down the vast list from literature, while still allowing a wide selection range of inhibitors. The list of the initial screening can be found in tables 4.1 to 4.3.

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Note: the criteria are not placed in a certain order of importance
<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>Substrate</th>
<th>Type</th>
<th>pH</th>
<th>Price(^a)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{NH}_4)_2\text{Ce(NO}_3\text{)}_6) + silane sol-gel</td>
<td>GA</td>
<td>Mixed</td>
<td>4</td>
<td>-</td>
<td>Sonification creates radicals, reducing Ce(^{4+}) ions, which polymerizes silane better.</td>
</tr>
<tr>
<td>1-(3-(4-Methylphenyl)-5-(quinoxalin-6-yl)-4,5-dihydropyrazol-1-yl)butan-1-one</td>
<td>Mild steel</td>
<td>Mixed</td>
<td>3</td>
<td>-</td>
<td>The quinoxaline derivate can compete with Cl(^-) and adheres by using its lonepairs or chemically bond with the steel surface.</td>
</tr>
<tr>
<td>2-Mercaptobenzothiazole</td>
<td>GA</td>
<td>Anodic</td>
<td>Neutral</td>
<td>€25.60</td>
<td>Creates complexes with metallic cations and adheres to SI. There is possible photodegradation.</td>
</tr>
<tr>
<td>3-Amino-1,2,3-triazole</td>
<td>HSLA</td>
<td>Mixed</td>
<td>Acidic</td>
<td>€139.00</td>
<td>ATA adheres to the surface, protecting it.</td>
</tr>
<tr>
<td>Actirox/Shieldex (Zn(PO(_4))_2Mo/Ca exchange silica)</td>
<td>GA, Zn</td>
<td>Cathodic</td>
<td>Neutral</td>
<td>-</td>
<td>Formation of a CaPO(_4) protective layer. The silicates may promote CaPO(_4) precipitation.</td>
</tr>
<tr>
<td>Benzotriazole</td>
<td>Galvanized steel</td>
<td>Anodic</td>
<td>Neutral</td>
<td>€60.40</td>
<td>Inhibitor for Cu, Al, Steel, Fe and Zn. Reacts with Zn(^{2+}) to form an unstable layer.</td>
</tr>
<tr>
<td>N,N-bis(phosphonomethyl) glycine + ZnSO(_4)+NaWO(_4)</td>
<td>Carbon steel</td>
<td>Mixed</td>
<td>Neutral to acidic</td>
<td>€59.50 + €36.70 + €69.50</td>
<td>BPMG reacts with Zn to form a dense layer. W reacts with Fe to form another layer. Zn forms hydroxides to precipitate on the cathodic sites.</td>
</tr>
<tr>
<td>Caffeine</td>
<td>Mild steel</td>
<td>Cathodic</td>
<td>Neutral</td>
<td>€40.40</td>
<td>Caffeine strongly bonds to steel surface, preventing cathodic reaction.</td>
</tr>
<tr>
<td>Ce(NO(_3))(_3)</td>
<td>Zinc plated steel</td>
<td>Cathodic</td>
<td>Neutral</td>
<td>€51.20</td>
<td>On cathodic sites, Ce(OH)(_3) and Ce(_2)O(_3)-H(_2)O forms. Further growing causes cracking and accelerates corrosion.</td>
</tr>
<tr>
<td>Ce(NO(_3))(_3) vinyltrimethoxysilane + HDG</td>
<td>Mixed</td>
<td>Neutral</td>
<td>€51.20 + €70.80</td>
<td>Steel is prepped in Ce(NO(_3))(_3) and a layer is formed. After dipping in silane, Si-O-Ce bonds form. Together a strong film is formed.</td>
<td></td>
</tr>
<tr>
<td>CeCl(_3)+H(_2)O</td>
<td>GA, Zn</td>
<td>Cathodic</td>
<td>Neutral</td>
<td>€65.60</td>
<td>A thin yellow film (Ce(^{4+})) forms. Too long exposure or too high concentrations are detrimental.</td>
</tr>
<tr>
<td>CoCl(_2)(_6)</td>
<td>GA, Zn</td>
<td>Cathodic</td>
<td>≈ 4.5</td>
<td>€104.00</td>
<td>Co behaves as an electron trap. Too high concentrations accelerates corrosion. The inhibitor is quite weak.</td>
</tr>
</tbody>
</table>

\(^a\)Prices are indicative based on 100 G of product and were obtained from http://www.sigmaaldrich.com. Note: prices were obtained on April 2016 and are subject to change. Ordering in industrial bulk scales will obviously decrease pricing.
<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>Substrate</th>
<th>Type</th>
<th>pH</th>
<th>Price(^a)</th>
<th>Comments</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ginger</td>
<td>Steel</td>
<td>Cathodic</td>
<td>Neutral</td>
<td>-</td>
<td>Ginger compounds adhere to the surface</td>
<td>[96]</td>
</tr>
<tr>
<td>La(4-NO(_2))Cl(_3)</td>
<td>Mild steel</td>
<td>Mixed</td>
<td>5-7</td>
<td>€150.00 (La(NO(_3))(_3))&lt;br&gt;€807 (cinnamate)</td>
<td>Initial iron carboxylate complexes form a layer. Due to increase in local pH, the RE hydrolysates, precipitates and forms an extra hydroxide layer.</td>
<td>[26, 119]</td>
</tr>
<tr>
<td>La(NO(_3))(_3)</td>
<td>HDG</td>
<td>Cathodic</td>
<td>Neutral</td>
<td>€150.00</td>
<td>A La(_2)O(_3)/La(OH)(_3) layer forms.</td>
<td>[109]</td>
</tr>
<tr>
<td>Na(_2)MoO(_4)</td>
<td>Mild steel</td>
<td>Anodic</td>
<td>7-8.5</td>
<td>€82.80</td>
<td>MoO(_4) consumes H(^+) in its reactions to reduce pitting, it also acts as a selective cation barrier. It shows synergism with other compounds.</td>
<td>[73, 74, 76, 122]</td>
</tr>
<tr>
<td>Na(_2)SiO(_3)</td>
<td>Mild steel</td>
<td>Anodic</td>
<td>Alkaline</td>
<td>€4.88</td>
<td>Forms a protecting film on the oxidizing iron surface.</td>
<td>[84]</td>
</tr>
<tr>
<td>Na(_2)WO(_4)</td>
<td>Cold rolled steel</td>
<td>Mixed</td>
<td>-</td>
<td>€69.50</td>
<td>Reacts with H(^+) to form hydroxide. Can react with Fe as well to form layer.</td>
<td>[86]</td>
</tr>
<tr>
<td>Na(_3)PO(_4)</td>
<td>Zn</td>
<td>Anodic</td>
<td>Neutral</td>
<td>€84.40</td>
<td>Precipitates on anodic sites.</td>
<td>[81]</td>
</tr>
<tr>
<td>Na(_2)NO(_3)</td>
<td>Mild steel</td>
<td>Anodic</td>
<td>8.5</td>
<td>€20.80</td>
<td>NO(_2) reacts with iron hydroxide to form iron oxide. Pitting is accelerated by H(^+) formation.</td>
<td>[76]</td>
</tr>
<tr>
<td>Na(_2)NO(_3) + Na(_2)B(_2)O(_4))(^b)</td>
<td>Low carbon steel</td>
<td>Anodic</td>
<td>5.9</td>
<td>€20.80 + €23.10</td>
<td>NO(_2) is adsorbed to the layer. Borax stabilises the pH and strengthens the NO(_3) bond.</td>
<td>[27]</td>
</tr>
<tr>
<td>Na(_2)V(_2)O(_7) + adipic acid</td>
<td>Mild steel</td>
<td>Anodic</td>
<td>Neutral</td>
<td>€75.20 + €21.10</td>
<td>Vanadium and adipic acid form an inhibiting layer (Fe complex) with the substrate.</td>
<td>[123]</td>
</tr>
<tr>
<td>Ni(_2)(OCO(_2))(_3)-4H(_2)O</td>
<td>GA, Zn</td>
<td>Cathodic</td>
<td>=6.5</td>
<td>€20.10</td>
<td>Ni behaves as an electron trap. Too high concentrations accelerate corrosion. The inhibition is quite weak and Ni easily leaches out.</td>
<td>[104]</td>
</tr>
<tr>
<td>Oleic imidazoline (N-b-hydroxyethyl oleyl imidazoline)</td>
<td>Iron</td>
<td>Mixed</td>
<td>-</td>
<td>€47.50 (500mg)</td>
<td>Forms a self-assembled system, longer immersion time gives better corrosion protection.</td>
<td>[91]</td>
</tr>
<tr>
<td>Paracetamol PO(_4) surfactant (C18A)</td>
<td>Carbon steel</td>
<td>Cathodic</td>
<td>-</td>
<td>€71.80</td>
<td>Paracetamol forms a protective layer. The current density is lowered by negatively charged phosphate heads on the cathodic cites. The donor-acceptor (\pi)-electrons from the P and O atoms provides chemical adsorption. The large chains attached on the groups reject water.</td>
<td>[92] [116]</td>
</tr>
</tbody>
</table>

\(^a\)Prices are indications based on 100 g of product and were obtained from https://www.sigmaaldrich.com. Note: prices were obtained on April 2016 and are subject to change. Ordering in industrial bulk scales will obviously decrease pricing.

This inhibitor can be found on the candidate list of REACH.

Table 4.2: List of the initial literature inhibitor screening (continued). Red indicates that the inhibitor was on the REACH list.
<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>Substrate</th>
<th>Type</th>
<th>pH</th>
<th>Price (€)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyvinyl alcohol (65000 g/mol) + KI</td>
<td>Mild steel</td>
<td>Mixed?</td>
<td>-</td>
<td>€18.76 + €28.6</td>
<td>Polyvinyl alcohol adheres to the surface chemically. The iodide ions stabilize this process and also acts as an inhibitor. Increased inhibition occurs at increasing temperatures.</td>
</tr>
<tr>
<td>TiO₂</td>
<td>Mild steel</td>
<td>Mixed</td>
<td>-</td>
<td>€10.76</td>
<td>Lone pairs of oxygen bonds to surface. Titanium oxide layer protects the metal.</td>
</tr>
<tr>
<td>TiOSO₄</td>
<td>Galvanized steel</td>
<td>Anodic</td>
<td>6.85</td>
<td>€25.20</td>
<td>TiOSO₄ dissolves into the liquid and forms TiO, because Ti²⁺ is unstable.</td>
</tr>
<tr>
<td>Y(NO₃)₃</td>
<td>HDG</td>
<td>Cathodic</td>
<td>Neutral</td>
<td>€131.00</td>
<td>A Y₂O₃/Y(OH)₃ layer forms.</td>
</tr>
<tr>
<td>Y(NO₃)₃ + Na₂SiO₃·H₂O</td>
<td>Carbon steel</td>
<td>Mixed</td>
<td>6</td>
<td>€131.00 + €4.88</td>
<td>Y forms a hydroxide/oxide layer on the cathodic site. Silicates react with the Fe ions in solution to form a layer.</td>
</tr>
</tbody>
</table>

Prices are indications based on 100g and were obtained from http://www.sigmaaldrich.com

Table 4.2: List of the initial literature inhibitor screening (continued): Red indicates that the inhibitor was on the REACH list.
The initial list from the literature screening is too long and needs to be further narrowed down. Therefore the following selection criteria were applied in order of importance:

1. **REACH** Legislation is an external factor that needs to be taken into account. Registration, Evaluation and Authorization of Chemicals (REACH) regulates the use of hazardous substances in the European Union. If a substance is on this list, it is prohibited from use by any company [21, 33]. Therefore, if the inhibitor is on the REACH list, it will be automatically excluded.

2. **Pricing** Pricing is of course one of the main criteria. Aim is to have the most optimal balance in price per unit and performance. Therefore, it is required to have an inhibitor that has a good price/weight ratio. The cut-off price was subjective to the people involved.

3. **Production scalability** It is obvious that if an inhibitor is not easily available or cannot be produced on an industrial scale, it cannot be used. La(4-NO2,cin)3 for example, needs to be synthesised and is not readily available in bulk size.

4. **Possibilities for synergism** If required and possible, it is preferable to have 1, 2 or extreme cases 3 inhibitors that can work synergistically. This can be achieved by taking into account if an inhibitor is anodic, cathodic, mixed or having an unique mechanism. For example, suppose the selection is composed of several inhibitors, because an inhibitor that worked for both substrates could not be found or all the inhibitors are weak. If inhibitors are selected on the possibility of synergism, the combined effects might compensate for an individual inhibitor.

Note: the criteria "long-term stability" was not applied, due to the fact that in literature it is usually not stated how effectively the researched inhibitor is on a long time scale.

By applying the above mentioned criteria and discussing with the people involved, 7 inhibitors were selected to be further studied, of which two are reference inhibitors (see tables 4.4 and 4.5). The reference inhibitors are the inhibitors that have high literature efficiencies and are frequently researched. These inhibitors will not be used, because it is known they have long term stability issues. The other selected inhibitors will be compared to these reference inhibitors when they are electrochemically evaluated. It must be noted that there were more candidates that fitted the criteria, but only a maximum of 7 inhibitors were allowed to be further evaluated. This was to reduce the workload that had to be done in the limited amount of time available.

Table 4.4: Preselection: Reference inhibitors. Numbers correspond to the applied criteria mentioned above.

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>Motivation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce(NO3)3</td>
<td>1. Is not stated in the REACH list.</td>
</tr>
<tr>
<td></td>
<td>2. €51.20/100 g</td>
</tr>
<tr>
<td></td>
<td>3. Bulk production is possible.</td>
</tr>
<tr>
<td></td>
<td>4. Has ability to work synergistically.</td>
</tr>
<tr>
<td></td>
<td><strong>Additional motivation:</strong> Cerium nitrate has been studied extensively in literature and gives notable inhibition. However, due to it having stability issues when used for longer periods, it will not be a candidate to be used as the final inhibitor, but as a reference inhibitor.</td>
</tr>
<tr>
<td>2-Mercaptobenzothiazole (MBT)</td>
<td>1. Is not stated in the REACH list. There is ongoing discussing about &quot;needs to be restricted&quot;.</td>
</tr>
<tr>
<td></td>
<td>2. €25.60/100 g</td>
</tr>
<tr>
<td></td>
<td>3. Bulk production is possible.</td>
</tr>
<tr>
<td></td>
<td>4. Has ability to work synergistically.</td>
</tr>
<tr>
<td></td>
<td><strong>Additional motivation:</strong> MBT is also extensively mentioned in literature and also provides excellent inhibition. Unfortunately, it is also known that this inhibitor has stability issues for the long term. Therefore MBT will be used as a reference inhibitor.</td>
</tr>
</tbody>
</table>
Table 4.5: Preselection: Inhibitors that past the selection criteria. Numbers correspond to the applied criteria mentioned above.

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>Motivation</th>
</tr>
</thead>
</table>
| KI        | 1. Is not stated in the REACH list.  
           | 2. €28.60/100 g  
           | 3. Bulk production is possible.  
           | 4. Has ability to work synergistically.  
           | **Additional motivation:** Potassium iodide inhibits corrosion at low pH values, which can occur locally (for example, in pits with Cl⁻). Furthermore, KI shows improved corrosion inhibition at elevated temperatures when combined with an organic inhibitor. (Note: Polyvinyl alcohol was not selected, due to the fact that it was difficult to get the same chain length). |
| Na₂MoO₄   | 1. Is not stated in the REACH list.  
           | 2. €82.80/100 g  
           | 3. Bulk production is possible.  
           | 4. Has ability to work synergistically.  
           | **Additional motivation:** The possible cation selective barrier makes sodium molybdate quite unique. It furthermore can consume H⁺ which aids in the protection against pitting. It also has very low toxicity. |
| Na₂SiO₃   | 1. Is not stated in the REACH list.  
           | 2. €4.88/100 g  
           | 3. Bulk production is possible.  
           | 4. Has ability to work synergistically.  
           | **Additional motivation:** Sodium metasilicate is very cheap poses a very low environmental risk. |
| Na₂WO₄    | 1. Is not stated in the REACH list.  
           | 2. €69.50/100 g  
           | 3. Bulk production is possible.  
           | 4. Has ability to work synergistically.  
           | **Additional motivation:** Sodium tungstate can consume H⁺ to form a layer, removing the corrosive species and increase passivity. |
| TiOSO₄    | 1. Is not stated in the REACH list.  
           | 2. €25.20/100 g  
           | 3. Bulk production is possible.  
           | 4. Has ability to work synergistically.  
           | **Additional motivation:** It is generally known that titanium has a very good passivity due to its oxide layer. Perhaps by applying inhibitors based on titanium, some of their passivation properties be conveyed to the substrate. TiOSO₄ gave one of the highest efficiencies compared to the other titanium based inhibitors. |
4.3. Electrochemical performance screening

To further narrow down the selection, linear sweep voltammetry has been applied, from which the corrosion current density was obtained. Those values were used to calculate inhibitor efficiencies, which on their turn were used to evaluate the inhibitors and make a final inhibitor selection (see figure 4.5 for the flow diagram).

![Figure 4.5: Flow diagram of the inhibitor screening with polarisation methods](image)

To perform the electrochemical screening procedure, an optimal inhibitor concentration for the substrates had to be found first. Therefore, an appropriate starting inhibitor concentration had to be selected. It was chosen to use an optimum inhibitor concentration (concentration which gave the highest inhibitor efficiency) from literature as the starting concentration (see table 4.6). This concentration would be presumably close to the optimum concentration for the substrates used in this report, based on the assumption that inhibitors in literature would roughly behave similar. This would provide a more efficient way to find the optimal concentration for the used substrates than starting with a standard concentration that would be applied to all inhibitors. After selecting the inhibitor concentrations from literature, additional concentrations were added to give a visualisation of the course of the inhibitor efficiency as a function of the inhibitor concentration. The additional concentrations would be twice or half of the literature concentration. In the case of sodium metasilicate and sodium tungstate, a half was not taken. This was due to the fact that this would result to very low concentrations, which were difficult to measure accurately with the providing equipment. For MBT, the literature concentration was already at maximum solubility, thus doubling the concentration was not possible. Furthermore, during experiments, it became clear that sodium molybdate, sodium metasilicate and sodium tungstate showed good inhibition and additional concentrations were needed to better evaluate the inhibitor. Note: for sodium tungstate also ten folds have been chosen, to see the results of more extreme cases.

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>Literature concentration</th>
<th>Additional concentrations</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(g/L)</td>
<td>(mM)</td>
<td>(g/L)</td>
</tr>
<tr>
<td>Ce(NO₃)³</td>
<td>20</td>
<td>46</td>
<td>10,40</td>
</tr>
<tr>
<td>KI</td>
<td>8.3</td>
<td>50</td>
<td>4,15</td>
</tr>
<tr>
<td>MBT</td>
<td>2</td>
<td>12</td>
<td>0.5,1</td>
</tr>
<tr>
<td>Na₂MoO₄</td>
<td>41</td>
<td>170</td>
<td>2.5,10,20,60</td>
</tr>
<tr>
<td>Na₂SiO₃</td>
<td>0.3</td>
<td>2.5</td>
<td>0.5,2.5</td>
</tr>
<tr>
<td>Na₂WO₄</td>
<td>0.1</td>
<td>0.3</td>
<td>0.5,2,20,40</td>
</tr>
<tr>
<td>TiO₂SO₄</td>
<td>30</td>
<td>187</td>
<td>10,60</td>
</tr>
</tbody>
</table>

### 4.3.1. Polarisation curves

After selecting the concentrations, LSV experiments were carried out. Polarisation plots for the inhibitors with their highest efficiencies are plotted in figure 4.6. To see the polarisation curves for all concentrations, see appendix A.1. For each substrate, the following will briefly be mentioned:

- The anodic/cathodic/mixed behaviour
- The indication of passivity
- Other observations made during experiments

The reference is defined as the bare substrate immersed in 0.05 M NaCl.
Figure 4.6: Polarisation curves for car underbody substrates: Inhibitors with their highest efficiencies versus the reference have been plotted. Numbers in the legend correspond to the inhibitor concentration. Note: oxotitanium sulphate curves are not included, due to this inhibitor not inhibiting. For the plots of the other concentrations, see appendix A.1.
GA steel

Cerium nitrate and potassium iodide showed little potential shift after anodic polarisation, respectively 30 mV and 40 mV (maximum shifts). This in junction with a corrosion current density shift suggests a mixed behaviour on GA steel. On the other hand, MBT, sodium molybdate, sodium metasilicate and sodium tungstate revealed a clear positive potential shift accompanied with a current corrosion density decrease. This implies an anodic behaviour for these inhibitors. Oxotitanium sulphate was the only inhibitor that exhibited a very different behaviour. Not only were the shifts in potential increased (30 g/L and 60 g/L) and decreases (10 g/L), it appears that the corrosion current density is increased a hundred fold from the reference. This implies an increase in corrosion, therefore TiOSO₄ is actually a corrosion accelerator.

Passivity could only be observed with sodium metasilicate. A passive region could be noticed at a concentration of 2 g/L and 5 g/L. This might be an indication of a strong passive layer that was formed on top of the substrate. This passive region is abruptly diminished at a -0.1 V vs SHE (2 g/L), probably due to break down of the layer. The 5 g/L concentration did not show a breakdown potential, but it might at higher potentials. The lower concentrations did show this passive behaviour. Oxotitanium sulphate displayed a peculiar behaviour at a concentration of 10 g/L, which resembled a breakdown potential. The curve became almost horizontal a certain potential, but a passive region could not be found. This sudden discontinuity in the curve does not occur at higher concentrations. Perhaps this breakdown is due to a corrosion product that only occurs at low concentration of TiOSO₄ or an unknown reaction occurs at the surface. An equipment error seemed unlikely, because the experiment was done in trifold and gave the same results.

Cerium nitrate and sodium tungstate showed the formation of a layer on top of the substrate. The layer of cerium nitrate was yellow pale, flaky and covered the whole substrate surface. The layer of sodium tungstate on the other hand was formed on specific spots (see figure 4.7). Despite the visible layer, both inhibitors did not reveal passivity in their polarisation curves. MBT revealed the formation of a colloid suspension which during polarisation settled down on the substrates. However, layer formation was not visible after finishing polarisation.

![Samples before and after exposure to LSV measurement with 40 g/L Na₃WO₄](image1.png)

Figure 4.7: Samples before and after exposure to LSV measurement with 40 g/L Na₃WO₄. Figure 4.7b shows little white spots which were made of very fine (almost powder like) particles which were easily removed with a jet of water. Note: lighting differs for each picture.

When the inhibitors sodium molybdate, sodium metasilicate and sodium tungstate were dissolved, an increase in pH occured, respectively, pH= 9, 12.3 and 9. Oxotitanium on the other hand, showed a pH decrease. The concentrations 10, 30 and 60 g/L gave, respectively, a pH of 1.2, 0.7, 0.5. After polarisation with TiOSO₄, it could be noticed that the surface of the substrates were severely tarnished. The zinc layer of the GA steel was completely removed and the underlying steel was also slightly corroded. Perhaps, during dissolution, the following reaction might have occurred:

\[
\text{TiOSO}_4 + 2\text{H}_2\text{O} \rightarrow \text{TiO(OH)}_2 + \text{H}_2\text{SO}_4
\]

The formation of sulfuric acid might explain the large decrease in pH and the colour change of the solution. According to the corresponding paper [107], the solution was adjusted to pH=2 with H₃PO₄.
Knowing that phosphates are also inhibitors and to only study oxotitanium sulphate, pH adjustments with $\text{H}_3\text{PO}_4$ were avoided. A small test was conducted to see if TiOSO$_4$ was inhibiting at neutral pH by adjusting the pH with NaOH. Corrosion greatly decreased, but inhibition was very weak (<20%). Furthermore, by adjusting the pH, the clear solution became a white opaque colloid suspension, which settled down at the bottom.

HSS

Cerium nitrate showed slight shifts (~50 mV) to negative potentials and a decrease in corrosion current density, indicating mixed cathodic inhibition. KI showed clear potential shift (~100 mV), but in the anodic as well as in the cathodic direction (see figure A.9). Concentrations below 8.3 g/L gave anodic inhibition, while concentrations above give cathodic inhibition. MBT exhibited a clear cathodic shift accompanied with a corrosion current density shift to lower currents, suggesting cathodic behaviour. Sodium molybdate, sodium metasilicate and sodium silicate expressed similar to GA steel a clear anodic behaviour. Just like GA steel, oxotitanium sulphate showed corrosion acceleration by having an increase in corrosion current density.

A clear passive region can be seen from the anodic curves of sodium molybdate with a break-down potential that lies roughly around +0.25 V vs SHE for all concentrations, which might indicate the formation of a strong passive layer. The curve in this the passive region also contains a lot of noise, indicating that the passive layer is continuously broken down and build up. In literature, this passive region with noise was also observed [73, 126]. The anodic curves of 2 g/L and 5 g/L of sodium metasilicate also exhibited a passive region with a lot of noise. The breakdown potential was not observed, due to the measurement boundaries that were set up. Of course, this might be observed at higher potentials. Unlike polarisation on GA steel, which did not express a clear passive region, on HSS sodium tungstate did show one starting from 20 g/L and containing a lot of noise. Of course, this might be observed at higher potentials. Unlike polarisation on GA steel, which did not express a clear passive region, on HSS sodium tungstate did show one starting from 20 g/L and containing a lot of noise.

Similar to GA steel, oxotitanium sulphate also revealed what looked like a potential breakdown without a clear sign of a passive region. This was however not found at higher concentrations.

Only cerium nitrate revealed a visible formation of a layer. Like on GA steel, this layer was flaky pale yellow and covered the whole substrate surface. Surprisingly, sodium tungstate did not show a visible layer on the HSS samples, which was observed with GA steel (see figure 4.7d).

4.3.2. Inhibitor efficiencies

Corrosion current densities were obtained from the LSV experiments by the usage of the Tafel tangents (see section 3.1.2). The obtained values were used to calculate the inhibitor efficiencies:

$$\eta = \frac{i_{\text{corr}} - i_{\text{inhib}}}{i_{\text{corr}}} \times 100\%$$

which are summarised in tables 4.7 and 4.8. The efficiencies have also been plotted versus concentration in figure 4.8.

Since cerium nitrate and MBT are the reference inhibitors, the inhibitor efficiencies should be compared with respect to these reference inhibitors. It can be clearly seen that MBT efficiencies are much higher than cerium nitrate efficiencies. Therefore, with respect to the inhibition efficiencies, MBT would be a more suitable reference inhibitor than cerium nitrate for both substrates.

From the tables, it is also clear that some inhibitors are effective on both substrates. Therefore, here the efficiencies will be discussed all together instead of per substrate.
<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>Conc. (g/L)</th>
<th>$E_{corr}$ (mV)</th>
<th>$b_a$ (mV/dec)</th>
<th>$b_c$ (mV/dec)</th>
<th>$i_{corr}$ ($\mu$Acm$^{-2}$)</th>
<th>$\sigma_{i_{corr}}$ ($\mu$Acm$^{-2}$)</th>
<th>$\eta$ (%)</th>
<th>$\sigma_\eta$ (%)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blanc</td>
<td></td>
<td>-552</td>
<td>94</td>
<td>-318</td>
<td>10.7</td>
<td>4</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Ce(NO$_3$)$_3$</td>
<td>10</td>
<td>-536</td>
<td>55</td>
<td>-227</td>
<td>6.6</td>
<td>4.4</td>
<td>39</td>
<td>29</td>
<td>White-yellow layer is visible after cathodic polarisation. At low potentials, the white layer becomes thicker, cracks and becomes flaky.</td>
</tr>
<tr>
<td></td>
<td>20*</td>
<td>-531</td>
<td>47</td>
<td>-163</td>
<td>6.6</td>
<td>7.1</td>
<td>39</td>
<td>44</td>
<td></td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>-532</td>
<td>53</td>
<td>-149</td>
<td>7.4</td>
<td>1.6</td>
<td>31</td>
<td>29</td>
<td></td>
</tr>
<tr>
<td>KI</td>
<td>4</td>
<td>-530</td>
<td>63</td>
<td>-467</td>
<td>8.5</td>
<td>2.9</td>
<td>20</td>
<td>10</td>
<td>Many pits are visible after polarisation.</td>
</tr>
<tr>
<td></td>
<td>8.5*</td>
<td>-530</td>
<td>72</td>
<td>-245</td>
<td>8.4</td>
<td>3.7</td>
<td>22</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>-561</td>
<td>57</td>
<td>-347</td>
<td>7.2</td>
<td>1.6</td>
<td>33</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td>MBT</td>
<td>0.5</td>
<td>-459</td>
<td>55</td>
<td>-341</td>
<td>3.0</td>
<td>2.3</td>
<td>72</td>
<td>60</td>
<td>Inhibitor has a low dissolvability. A layer of suspension covers the WE during measurements.</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>-486</td>
<td>54</td>
<td>-409</td>
<td>3.8</td>
<td>1.2</td>
<td>65</td>
<td>32</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2*</td>
<td>-557</td>
<td>89</td>
<td>-372</td>
<td>1.4</td>
<td>1</td>
<td>87</td>
<td>67</td>
<td></td>
</tr>
<tr>
<td>Na$_2$MoO$_4$</td>
<td>2</td>
<td>-323</td>
<td>38</td>
<td>-5763</td>
<td>3.0</td>
<td>1.1</td>
<td>72</td>
<td>38</td>
<td>Small pits visible, even at high inhibition.</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>-304</td>
<td>19</td>
<td>-1169</td>
<td>3.8</td>
<td>1.6</td>
<td>65</td>
<td>36</td>
<td>Inhibitor solution is alkaline (pH=9).</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>-452</td>
<td>58</td>
<td>-466</td>
<td>3.2</td>
<td>0.8</td>
<td>70</td>
<td>32</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>-282</td>
<td>42</td>
<td>-5508</td>
<td>6.2</td>
<td>2.5</td>
<td>42</td>
<td>23</td>
<td></td>
</tr>
<tr>
<td></td>
<td>41*</td>
<td>-353</td>
<td>52</td>
<td>-723</td>
<td>2.3</td>
<td>1.5</td>
<td>79</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>-347</td>
<td>64</td>
<td>-1713</td>
<td>2.4</td>
<td>0.4</td>
<td>77</td>
<td>31</td>
<td></td>
</tr>
<tr>
<td>Na$_2$SiO$_3$</td>
<td>0.3*</td>
<td>-409</td>
<td>50</td>
<td>-3397</td>
<td>4.6</td>
<td>2.0</td>
<td>57</td>
<td>33</td>
<td>Inhibitor solution is alkaline (pH=12.5).</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>-546</td>
<td>102</td>
<td>-397</td>
<td>2.7</td>
<td>1.2</td>
<td>75</td>
<td>44</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>-332</td>
<td>536</td>
<td>-386</td>
<td>0.5</td>
<td>0.1</td>
<td>96</td>
<td>37</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>-358</td>
<td>742</td>
<td>-433</td>
<td>1.9</td>
<td>0.2</td>
<td>83</td>
<td>31</td>
<td></td>
</tr>
<tr>
<td>Na$_2$WO$_4$</td>
<td>0.1*</td>
<td>-405</td>
<td>52</td>
<td>-780</td>
<td>8.5</td>
<td>3.2</td>
<td>21</td>
<td>11</td>
<td>At certain spots a white layer is visible, which can be easily removed with a jet of water. Inhibitor solution is alkaline (pH=9).</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>-424</td>
<td>47</td>
<td>-1013</td>
<td>6.9</td>
<td>3.2</td>
<td>36</td>
<td>21</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>-369</td>
<td>31</td>
<td>-3266</td>
<td>3.9</td>
<td>1.6</td>
<td>64</td>
<td>36</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>-364</td>
<td>63</td>
<td>-2941</td>
<td>3.1</td>
<td>0.7</td>
<td>71</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>-298</td>
<td>73</td>
<td>-1824</td>
<td>4.8</td>
<td>2.4</td>
<td>55</td>
<td>34</td>
<td></td>
</tr>
<tr>
<td>TiOSO$_4$</td>
<td>10</td>
<td>-667</td>
<td>465</td>
<td>-169</td>
<td>163.7</td>
<td>12.9</td>
<td>-1426</td>
<td>-538</td>
<td>After anodic polarisation, the zinc layer has been completely removed. Solution was acidic (pH=0.5-1.2).</td>
</tr>
<tr>
<td></td>
<td>30*</td>
<td>-263</td>
<td>427</td>
<td>-603</td>
<td>1024.7</td>
<td>145.9</td>
<td>-9454</td>
<td>-3739</td>
<td></td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>-304</td>
<td>477</td>
<td>-394</td>
<td>746.7</td>
<td>73.1</td>
<td>-6862</td>
<td>-2620</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.7: Results of the inhibitors selected by criteria for C2 steel. Inhibitor efficiency, $\eta$, is calculated with equation 4.13. $E_{corr}$, vs. SHE. All indicates the optimum concentration found in literature.
### Table 4.2: Results of LSV measurements of the inhibitors selected by criteria for HSS. An indicator indicates the optimum concentration found in literature.

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>Conc.</th>
<th>$E_{corr}$</th>
<th>$b_a$</th>
<th>$b_c$</th>
<th>$i_{corr}$</th>
<th>$\sigma_{i_{corr}}$</th>
<th>$\eta$</th>
<th>$\sigma_\eta$</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(g/L)</td>
<td>(mV)</td>
<td>(mV/dec)</td>
<td>(mV/dec)</td>
<td>($\mu$A cm$^{-2}$)</td>
<td>($\mu$A cm$^{-2}$)</td>
<td>(%)</td>
<td>(%)</td>
<td></td>
</tr>
<tr>
<td>Blanc</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>-395</td>
<td>-333</td>
<td>17.9</td>
<td>6.7</td>
<td>28</td>
<td>12</td>
<td></td>
<td></td>
<td>White-yellow layer is visible after cathodic polarisation. At low potentials, the white layer becomes thicker, cracks and becomes flaky.</td>
</tr>
<tr>
<td>20</td>
<td>-349</td>
<td>-547</td>
<td>16.3</td>
<td>6.7</td>
<td>35</td>
<td>16</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>-414</td>
<td>-350</td>
<td>16.8</td>
<td>8.1</td>
<td>33</td>
<td>17</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KI</td>
<td>4</td>
<td>-262</td>
<td>-453</td>
<td>13.4</td>
<td>3.6</td>
<td>46</td>
<td>16</td>
<td>10</td>
<td>Many small pits visible after polarisation.</td>
</tr>
<tr>
<td>8.3*</td>
<td>-395</td>
<td>-348</td>
<td>19.0</td>
<td>3.8</td>
<td>24</td>
<td>7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>-485</td>
<td>-2881</td>
<td>23.9</td>
<td>2.2</td>
<td>4</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MBT</td>
<td>0.5</td>
<td>-403</td>
<td>-202</td>
<td>5.4</td>
<td>3.9</td>
<td>78</td>
<td>58</td>
<td>10</td>
<td>Inhibitor has a low dissolvability. A layer of suspension covers the WE during measurements.</td>
</tr>
<tr>
<td>1</td>
<td>-309</td>
<td>-1042</td>
<td>11.1</td>
<td>6.8</td>
<td>55</td>
<td>36</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2*</td>
<td>-396</td>
<td>-241</td>
<td>1.9</td>
<td>0.4</td>
<td>92</td>
<td>28</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na$_2$MoO$_4$</td>
<td>2</td>
<td>68</td>
<td>187</td>
<td>-852</td>
<td>5.8</td>
<td>1.3</td>
<td>77</td>
<td>24</td>
<td>Small pits visible, even at high inhibition. Inhibitor solution is alkaline (pH=9).</td>
</tr>
<tr>
<td>5</td>
<td>3</td>
<td>424</td>
<td>-143</td>
<td>0.3</td>
<td>0.1</td>
<td>99</td>
<td>55</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>14</td>
<td>912</td>
<td>-213</td>
<td>0.5</td>
<td>0.1</td>
<td>98</td>
<td>24</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>-13</td>
<td>423</td>
<td>-135</td>
<td>0.4</td>
<td>0.1</td>
<td>98</td>
<td>39</td>
<td></td>
<td></td>
</tr>
<tr>
<td>41*</td>
<td>75</td>
<td>451</td>
<td>-154</td>
<td>0.3</td>
<td>0.1</td>
<td>99</td>
<td>46</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>-13</td>
<td>411</td>
<td>-120</td>
<td>0.2</td>
<td>0.0</td>
<td>99</td>
<td>28</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na$_2$SiO$_3$</td>
<td>0.3*</td>
<td>-194</td>
<td>265</td>
<td>-898</td>
<td>13.5</td>
<td>0</td>
<td>46</td>
<td>0</td>
<td>Inhibitor solution is alkaline (pH=12.5).</td>
</tr>
<tr>
<td>0.5</td>
<td>-80</td>
<td>202</td>
<td>-610</td>
<td>3.7</td>
<td>1.2</td>
<td>85</td>
<td>33</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>-130</td>
<td>832</td>
<td>-145</td>
<td>0.5</td>
<td>0.2</td>
<td>98</td>
<td>40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>-101</td>
<td>362</td>
<td>-164</td>
<td>0.2</td>
<td>0.1</td>
<td>99</td>
<td>47</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na$_2$WO$_4$</td>
<td>0.1*</td>
<td>-148</td>
<td>222</td>
<td>-1605</td>
<td>20.7</td>
<td>0.7</td>
<td>17</td>
<td>4</td>
<td>Inhibitor solution is alkaline (pH=9).</td>
</tr>
<tr>
<td>0.5</td>
<td>-165</td>
<td>205</td>
<td>-1367</td>
<td>13.2</td>
<td>1.0</td>
<td>47</td>
<td>11</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>-41</td>
<td>230</td>
<td>-1317</td>
<td>9.7</td>
<td>0.7</td>
<td>61</td>
<td>14</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>3</td>
<td>557</td>
<td>-167</td>
<td>0.5</td>
<td>0.1</td>
<td>98</td>
<td>29</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>-5</td>
<td>641</td>
<td>-140</td>
<td>0.6</td>
<td>0.2</td>
<td>98</td>
<td>44</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiOSO$_4$</td>
<td>10</td>
<td>-293</td>
<td>534</td>
<td>-440</td>
<td>144.3</td>
<td>16.3</td>
<td>-479</td>
<td>115</td>
<td>Solution was acidic (pH=0.5-1.2).</td>
</tr>
<tr>
<td>30*</td>
<td>-301</td>
<td>211</td>
<td>-301</td>
<td>59.28</td>
<td>264.1</td>
<td>-2280</td>
<td>1125</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>-239</td>
<td>244</td>
<td>-365</td>
<td>781.3</td>
<td>259.1</td>
<td>-3037</td>
<td>1195</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
4.3. Electrochemical performance screening

Figure 4.8: Efficiency versus concentration for the used inhibitors: Orange line represents HSS, blue line represents GA steel. The dashed circle indicates the most optimal concentration.
Cerium nitrate showed a maximum inhibition around 20 g/L for both substrates and the curves per substrate seem to behave similarly. Potassium iodide behaved differently for each substrate. Increasing the concentrations correlates to an increasing inhibition on GA steel, whereas this is the opposite on HSS. The inhibition is however subpar compared to MBT values. MBT gave a minimum inhibition at 1 g/L for both substrate. Like potassium iodide, the curves for each substrate resemble each other.

Sodium molybdate gave a fluctuating inhibition curve for GA steel, whereas for HSS this curve resembled a classic Langmuir growth (see figure 4.9) [127]. Inhibition for GA steel are around MBT levels with sodium molybdate, whereas on HSS this inhibition is much higher (max 99%).

Sodium metasilicate also expressed a Langmuir type behaviour for both substrates. The inhibition was above MBT efficiencies if concentrations above 2 g/L are used. Langmuir behaviour was also observed with sodium tungstate, albeit the maximum are not the same for both substrates. On GA steel, the maximum inhibition is around MBT level (≈70%), whereas on HSS the efficiency reaches up to 99%.

As already predicted from the polarisation curves, oxotitanium sulphate was a corrosion accelerator. Large negative efficiencies can be seen for both substrates. However, HSS was more resistant against the inhibitor.

An optimal concentration for each inhibitor can be deduced from figure 4.8 by taking the following into account:

- The efficiency must by high for both inhibitors
- The amount of inhibitor must be minimized

As an example, the optimal concentration for potassium iodide is explained. From figure 4.8b, the optimal concentration would be 4 g/L. This concentration uses the least amount of potassium iodide and also grants the highest possible inhibition for HSS. The other concentrations requires more substance and less inhibition for one of the two substrates.

The optimal concentration is summarised in table 4.9.

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>Optimal concentration</th>
<th>$\eta_{GA}$ (%)</th>
<th>$\eta_{HSS}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce(NO$_3$)$_3$</td>
<td>10</td>
<td>39</td>
<td>28</td>
</tr>
<tr>
<td>KI</td>
<td>4</td>
<td>20</td>
<td>46</td>
</tr>
<tr>
<td>MBT</td>
<td>2</td>
<td>87</td>
<td>92</td>
</tr>
<tr>
<td>Na$_2$MoO$_4$</td>
<td>5</td>
<td>65</td>
<td>99</td>
</tr>
<tr>
<td>Na$_2$SiO$_3$</td>
<td>2</td>
<td>96</td>
<td>98</td>
</tr>
<tr>
<td>Na$_2$WO$_4$</td>
<td>20</td>
<td>71</td>
<td>98</td>
</tr>
</tbody>
</table>

Table 4.9: The optimal concentration per inhibitor for both substrates: Note: oxotitanium sulphate is not shown, due to it not inhibiting corrosion.

Figure 4.9: Example Langmuir growth
It must be noted that it was also possible to choose an optimal concentration per substrate rather than for both substrates. This was not chosen, because it was kept in mind that the final inhibitor has an industrial application: needing only one concentration makes it easier to standardize the application process, which is more cost efficient.

### 4.3.3 Final inhibitor selection

For the final inhibitor selection, the inhibitor efficiencies have been compared to the reference inhibitor (MBT) with table 4.9. It is clear from the table that cerium nitrate and potassium iodide are not potent inhibitors and therefore are discarded. Sodium tungstate and sodium molybdate both have comparable efficiencies, but they differ in optimal concentration. Industry requires the lowest concentration, therefore sodium tungstate is discarded as well. Finally, it seems obvious from the table that sodium metasilicate is the best inhibitor, but to obtain a more conscientious decision, sodium molybdate and sodium metasilicate will be compared to each other. A summary about these two inhibitors can be found in tables 4.10.

**Table 4.10: Comparison of the two final inhibitors**

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>Pro</th>
<th>Contra</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂MoO₄</td>
<td>• High solubility</td>
<td>• Alkaline (pH≈9), can affect ED coating</td>
</tr>
<tr>
<td></td>
<td>• Low environmental risk</td>
<td>• Relatively expensive (€52.30/100g)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Average GA steel inhibition</td>
</tr>
<tr>
<td>Na₂SiO₃</td>
<td>• High inhibition for both substrates</td>
<td>• Alkaline (pH≈12.3), can affect ED coating</td>
</tr>
<tr>
<td></td>
<td>• Requires a low concentration</td>
<td>• May cause respiratory irritation in powder form</td>
</tr>
<tr>
<td></td>
<td>• Inexpensive (€4.88/100g)</td>
<td></td>
</tr>
</tbody>
</table>

Besides performing better in inhibition and requiring a lower concentration, sodium metasilicate also has a lower price per unit compared to sodium molybdate. It seems obvious to choose for sodium metasilicate, however, some information about the long-time inhibition efficiency is required still. The LSV data was obtained after an immersion of 30 minutes, which gives information about short times. It is possible that initially an inhibitor works very well, but loses its effectiveness as time progresses. Therefore, an immersion experiment was conducted, to have a visually indication of the inhibition performance in time for the two inhibitors. The samples of GA steel and HSS were immersed for 8 weeks in varying concentration of sodium molybdate or sodium metasilicate (see figure 4.11).

The concentration series revealed that sodium molybdate failed to protect GA steel after 8 weeks. For all concentrations, corrosion products can be clearly seen. The HSS substrates showed better corrosion resistance with sodium molybdate. Concentrations above 80 g/L showed the least amount of red rust, but with 99% inhibition efficiency (from polarisation experiments) it was expected that no sign of red rust was visible at all. In contrast, sodium metasilicate demonstrated stable corrosion protection for both substrate. GA steel substrate showed white brittle corrosion products, but the amount decreases as the concentration is increased. Above 10 g/L, the zinc layer turns darker in colour (20 g/L initially gave a transparent film, but became white opaque after the film dried). For HSS, the inhibitor concentrations above 1 g/L almost fully protected the HSS substrate. Although, there was some small spots of local corrosion products still visible. Surprisingly, at high concentrations of silicate (>10 g/L), a gel like substance formed, but still protected the steel.

From this experiment, it is clear that sodium metasilicate shows a better inhibition perfromance in time than sodium molybdate. Thus overall, sodium metasilicate is the superior choice.
Figure 4.10: Immersion experiment: GA steel samples were immersed for 8 weeks in varying sodium molybdate or sodium metasilicate solutions containing 0.05 M NaCl.

Figure 4.11: Immersion experiment: HSS samples were immersed for 8 weeks in varying sodium molybdate or sodium metasilicate solutions containing 0.05 M NaCl.
4.4. Conclusions

An inhibitor literature screening has been performed which resulted in a list of 30 inhibitors. Next, a selection based on REACH, pricing, product scalability and possibilities for synergism have been applied. Eventually, 7 inhibitors remained and were subjected to polarisation experiments to be evaluated based on their electrochemical performance. From those 7, one inhibitor was superior compared to the others. With high inhibition efficiencies for both substrates, the low concentration of inhibitor that is required to obtain the high efficiencies, the relatively low price and having a good visible indication of long time inhibition performance, Na$_2$SiO$_3$ is the best inhibitor to prevent car underbody corrosion. This inhibitor will therefore be further studied to understand its mechanism for the substrates in this research.
Corrosion inhibitor mechanism study

This chapter will cover the study about the corrosion protecting mechanism of Na$_2$SiO$_3$. Adsorption models, surface analysis and electrochemical analysis will be presented to support the proposed mechanism. Finally, all the data will be put together to explain the mechanism.

5.1. Research approach

Having found the best corrosion inhibitor for GA steel and HSS under the conditions mentioned in this report, the question that rises is: What is the corrosion inhibition mechanism of sodium metasilicate? To answer that question, five different techniques have been chosen:

- **Adsorption isotherms** fitting can provide insight into the adsorption mechanism, which can be used to give an initial idea how the inhibition system works. It is a rather simple method which uses data which was already obtained during the LSV screening.

- **Surface analysis:**
  - **SEM & EDS** can provide visual evidence for the formation of a layer on top of the substrate. Furthermore, **EDS mapping** can possible reveal preferential sites on which a layer is formed.
  - **FTIR** provides knowledge about the chemical bonds present on top of the metal surface and can also reveal if there is a layer being formed.

- **Electrochemical analysis:**
  - **LSV** measurements can reveal inhibitor preferential sites on an electrochemical point of view. It also provides insight into the effect of the alkaline environment that accompanies the addition of sodium metasilicate in solution.
  - **EIS** allows observation of the electrochemical processes on the corroding surface in time. The impedance data can also be fitted to a model, which can describe the inhibition system.

The following sections will treat the mentioned techniques in the same order.
5.2. Adsorption isotherms

As already mentioned in section 2.3, inhibitors can form a layer on top of the substrate to protect it against corrosion. The process in which atoms, ions or molecules from the gas, liquid or dissolved solid adhere to the surface and form a film is called adsorption. Generally, adhesion is an equilibrium process, which can be described as:

\[
\text{adsorbate} + \text{adsorbent} \xrightleftharpoons{\text{adsorption}} \xrightarrow{\text{adsorption}} \text{adsorption} \xrightleftharpoons{\text{desorption}} \text{desorption}
\]  

(5.1)

One can predict the nature of adsorption by the usage of the so-called adsorption isotherms. In this case, the amount adsorbate on the adsorbent as a function of the inhibitor concentration at a constant temperature is plotted. The plot (= experimental data) is then compared with models that describe the adsorption. The usage of adsorption isotherms is very useful in discussing the adsorption process and it gives detailed information on adsorption mechanisms with relatively easy experiments.

To obtain the isotherm, the fractional coverage value, \( \theta \), must be calculated from \( \eta \), the inhibitor efficiency [27]:

\[
\theta = \frac{\eta}{100}
\]  

(5.2)

The \( \theta \) values should be fitted to various adsorption isotherm models to find the most appropriate isotherm. In literature, many isotherm models exist [127–129]. Here, the Langmuir, Freundlich and Temkin models have been used with the least squares method. The motivation to apply these models are given below.

**Langmuir**  
During LSV experiments, it was noticed that passivity occurred in the plots. However, a visible layer was not observed on the substrates and this suggests the formation of very thin layer, perhaps a monolayer. The Langmuir model is therefore used, as it is commonly used to qualitatively describe the formation of a monolayer. This model assumes that the substrate is perfectly flat and that all sites are equivalent. Each site can only hold one molecule, ion or atom, thus describing a monolayer. Furthermore, it is assumed that there are negligible or no interactions at all between adsorbates on adjacent sites. Of course, these are oversimplifications that do not usually hold in real systems. Nevertheless, the model is simple and does provide information that can be used to support other research methods. The equation is [27, 89, 128]:

\[
C \cdot k_{\text{ads}} = \frac{\theta}{1-\theta}
\]  

(5.3)

which can be linearized in the form:

\[
\frac{C}{\theta} = \frac{1}{k_{\text{ads}}} + C
\]  

(5.4)

with \( C \) the inhibitor concentration in g/L and \( k_{\text{ads}} \) the adsorption constant. The Langmuir model is plotted in figure 5.1a.

**Freundlich**  
Some papers have suggested a multilayer protection by sodium metasilicate [165]. Therefore, the Freundlich model is used as it gives an empirical description of adsorption which also accounts for multilayers, a rough surface and multisite adsorption. The equation can be formulated as [128, 130, 131]:

\[
\theta = k_{\text{ads}} \cdot C^{\frac{1}{n}}
\]  

(5.5)

and in linear form:

\[
\log(\theta) = \log(k_{\text{ads}}) + \frac{1}{n} \log(C)
\]  

(5.6)

with \( C \) the inhibitor concentration in g/L, \( k_{\text{ads}} \) the adsorption constant and \( n \) is an empirical parameter related to the adsorption intensity. The Freundlich model is plotted in figure 5.1b.
5.2. Adsorption isotherms

![Langmuir isotherm](image1)

- **Langmuir isotherm**
  - GA: \( y = 3.1834x + 0.0002 \), \( R^2 = 0.9938 \)
  - HSS: \( y = 0.9951x + 0.0018 \), \( R^2 = 0.9964 \)

![Freundlich isotherm](image2)

- **Freundlich isotherm**
  - GA: \( y = 0.2203x + 0.3564 \), \( R^2 = 0.8210 \)
  - HSS: \( y = 0.1203x + 0.1465 \), \( R^2 = 0.5941 \)

![Temkin isotherm](image3)

- **Temkin isotherm**
  - GA: \( y = 0.3945x + 1.5787 \), \( R^2 = 0.9854 \)

Figure 5.1: Various isotherms for GA steel and HSS in various \( \text{Na}_2\text{SiO}_3 \) concentration in 0.05 M \( \text{NaCl} \) solution. The \( \theta \) values and concentrations of \( \text{Na}_2\text{SiO}_3 \) were obtained from previous LSV data (see tables 4.7 and 4.7).

**Temkin**  When a layer is forming, it is not sure if the adsorbates interact with each other or not. Silicates, an ionic form of sodium silicate, are known to polymerize in solution. Thus adsorbates could interact with each other. The Temkin model can reveal this by taking the adsorbate-adsorbate interaction into account. It assumes that the heat of adsorption decreases linearly with increasing coverage. The equation is [130–132]:

\[
C \cdot k_{ads} = e^{\alpha \theta}
\]  \hspace{1cm} (5.7)

, or in linear form:

\[
\theta = \frac{1}{\alpha} \ln(C) + \frac{1}{\alpha} \ln(k_{ads})
\]  \hspace{1cm} (5.8)

, with \( C \) the inhibitor concentration in g/L, \( k_{ads} \) the adsorption constant and \( \alpha \) the interaction parameter. The Temkin model is plotted in figure 5.1c.

From figure 5.1 the regression values for each model can be found. The closer \( R^2 \) is to unity, the better the fit. The Langmuir isotherm has the highest \( R^2 \) value, for GA steel as well as for HSS. Therefore, it can be assumed that \( \text{Na}_2\text{SiO}_3 \) obeys the Langmuir adsorption isotherm. This finding is supported by several papers about sodium (meta)silicates as an inhibitor [125, 133, 134]. Based on the isotherm, one could assume that \( \text{Na}_2\text{SiO}_3 \) forms a monolayer, that the adsorption is quite homogenous and that there are no interaction between adsorbates.

The Langmuir model also allows the determination of the activation energy for adsorption. The \( k_{ads} \) can be related to the standard free energy of adsorption described by [27, 133, 135]:

\[
k_{ads} = \frac{1}{55.5} \exp \left( \frac{-\Delta G_{ads}}{RT} \right)
\]  \hspace{1cm} (5.9)

, which can be rewritten to obtain the adsorption activation energy:

\[
\Delta G_{ads} = -RT \ln(55.5k_{ads})
\]  \hspace{1cm} (5.10)
, with the value 55.5 is the concentration of water in mol/L, \( R \) the gas constant and \( T \) the absolute temperature.

The calculated values are summarised in Table 5.1.

Table 5.1: Thermodynamic adsorption parameters of \( \text{Na}_2\text{SiO}_3 \) on Toyota substrates: Values obtained from applying a Langmuir adsorption isotherm, with \( C=2 \) \( \text{g/L} \), \( T=293 \) \( \text{K} \), \( R=8.314 \). Note: \( k_{ads} \) is calculated from the b-intercept from the trendline.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>( R^2 )</th>
<th>( k_{ads} )</th>
<th>( \Delta G_{ads} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>GA steel</td>
<td>0.9938</td>
<td>5000</td>
<td>-30.5</td>
</tr>
<tr>
<td>HSS</td>
<td>0.9964</td>
<td>555.5</td>
<td>-25.2</td>
</tr>
</tbody>
</table>

For GA steel, the calculated activation energy comes close to the values from Chang et al. [136]. Their solution, containing 1 M NaOH and 0.1 M metasilicate, gave an activation energy of 36.7 kJ/mol with a rotation speed of 600 rpm. The solutions used in this report have lower pH and lower concentration, but extrapolating from their results, it seems that the obtained GA values are in the approximate range.

The data for HSS comes close to the values obtained by Anaee et al. [133]. They tested on their mild steel metasilicate and also fitted a Langmuir isotherm. At a concentration of 0.01 M, they obtained an activation energy of -27.9559 kJ/mol. Extrapolating their data gave, for a concentration of 16.3 mM, an activation energy of -26 kJ/mol, which comes close to the values for HSS.

The activation energy, \( \Delta G_{ads} \), indicates if the adsorption of the inhibitor is spontaneous and if the formed layer is stable. Large negative values suggest a spontaneous and very stable layer. Values around or less negative than -20 kJ/mol characterize physisorption [28, 89, 90, 135]; forces which are based on intermolecular forces (van der Waals forces, H-bonds). Physisorption is generally weak, non-specific and has a high forming rate. On the other hand, values around or more negative than -40 kJ/mol characterize chemisorption; forces based on the formation on the exchange of electrons; covalent bonds, which are generally strong and specific. The formation of a layer is generally slow at low temperatures, whereas at high temperatures, layer formation is fast.

In the present work, it seems that the layer formation is spontaneous and stable, but lies in the borderline between physisorption and chemisorption. Furthermore, the adsorption activation energies suggest that the inhibitor will adsorb stronger on GA steel than on HSS.

It must be emphasized that the Langmuir model is only applied on LSV data obtained after 30 minutes. Therefore, the conclusions made are only applicable in this short period. If time elapses, it is still possible that multiple layers can form and that adsorbate-adsorbate interaction occurs.

Conclusions
The following conclusions have been drawn:

- By fitting LSV data with various adsorption isotherm models, the Langmuir models was the most appropriate one. Therefore, sodium metasilicate obeys the Langmuir adsorption isotherm.

- The Langmuir model predicts a spontaneous monolayer with homogenous adsorption and no interaction between adsorbates.

- Thermodynamic calculations showed that adsorption activation energy for GA steel is more negative than for HSS. This suggests that inhibitor adsorption on GA steel is stronger than on HSS.
5.3. Surface analysis

5.3.1. SEM & EDS measurements

SEM & EDS measurements were carried out to determine if there was a layer formed on top of the metal substrates. SEM can provide visual evidence of a layer, whereas EDS can reveal if new elements have been deposited on the surface. Additionally, EDS can create elemental mappings, which can reveal where layers are deposited on the surface.

Figures 5.2 and 5.5 show, respectively, the SEM images of the surface of the GA steel samples and the HSS samples.

**GA steel**  On large magnifications (see figure 5.2a), a rough surface can be observed consisting of light and dark spots spanning the whole surface. Higher magnifications (see figure 5.6a) reveal that the light spots are build-up of crystals with an average length of 10 μm, whereas the darker spots are smooth surfaces. EDS point measurements for these areas reveal that there is very little difference between the two phases. According to the literature, the crystalline areas are the ζ phases (FeZn13) and the smooth areas are the same, but compressed during temper rolling process to increase surface quality [138, 140]. Hairline microcracks (not shown) can also be found on the GA steel surface, which are typical for zinc alloy coatings [17]. During heat treatment of the galvanized steel to form galvannealed steel, internal stresses of the coating develop and can cause cracking.

The 168h inhibitor treated samples reveal no significant alterations of the surface (see figure 5.2c). No indications of a silicate layer were visible. Most samples did not show corrosion products, but on some samples, localized white brittle corrosion products could be found (see figure 5.4a). EDS measurements have shown that this corrosion product mainly consists of Si, O and Zn and traces of Fe, C and Cl. EDS point measurements (see figure 5.3) revealed an increase in silicon levels from around 0wt% to 0.4-1.2wt%.

EDS mapping has been made for the 168h inhibitor treated GA steel samples (see figure 5.2e). The black areas have been found to be caused by ridges occurring on the sample (see appendix B.1) for proof) According to the literature, the lighter elements (Z<11) cannot be detected accurately and can be easily influenced by contamination [141, 142]. Despite the black areas caused by the ridges, it appears that the increase in silicon content is homogenous and no preferential sites could be detected.

Bare GA steel samples have also been exposed to 0.05 M NaCl without inhibitor for 168h (see figure 5.4b). Here, a layer of spherical corrosion products are scattered on the whole surface. The layer appears to be porous, as it is possible to detects the underlying substrate. The corrosion products are not homogenously spread, as there are localized spots visible. The white spherical colloids have been identified by EDS as zinc oxides. These oxides have not been found on inhibited samples and also differ from the localised corrosion products mentioned earlier.

**HSS**  Low magnification reveal a rough surface (see figure 5.5a), which on higher magnification can be seen as a surface consisting of ridges (see figure 5.5b). In between those ridges, pore like structures and micro cracks can be observed.

In contrast to GA steel findings, the 168 hours inhibitor treated HSS samples revealed an increase in microcracks spread across the surface (see figure 5.5d). The pore like structures observed before treatment are less present with inhibitor treatment. Corrosion products were not observed on inhibited samples. EDS point measurement (see figure 5.6) revealed an increase in silicon and oxygen levels from around, respectively, 0.2wt% to 1wt% and 0.2wt% to 0.9wt%.

An EDS mapping has also been made for the 168h inhibitor treated HSS samples (see figure 5.5e). Similar to GA steel, the increased silicon content is homogenous spread and no preferential sites could be detected.

Bare HSS samples have also been exposed to 0.05 M NaCl without inhibitor for 168h (see figure 5.7). Here, a fine porous layer of corrosion products are scattered on the whole surface. This layer has been identified by EDS as iron oxide. These corrosion products could not be found on inhibited samples.
Figure 5.2: SEM images GA steel
5.3. Surface analysis

Figure 5.3: EDS point measurements on GA steel samples. Measured points are highlighted with a red circle.

Table 5.2: Composition of the selected points according to the EDS measurements

<table>
<thead>
<tr>
<th>Point</th>
<th>O</th>
<th>Si</th>
<th>Fe</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>012 (Reference)</td>
<td>0.14±0.12</td>
<td>-</td>
<td>7.34±0.58</td>
<td>83.43±2.19</td>
</tr>
<tr>
<td>005 (168h)</td>
<td>0.87±0.09</td>
<td>0.62±0.14</td>
<td>7.72±0.47</td>
<td>85.56±1.76</td>
</tr>
</tbody>
</table>

Figure 5.4: SEM images of found corrosion products

(a) Localised corrosion product found on 168h inhibited sample (30x)
(b) Zinc oxide formed on 168h immersed sample (330x)
5. Corrosion inhibitor mechanism study

(a) Untreated sample (80x)  
(b) Untreated (2000x)  
(c) 168h inhibitor treated sample (80x)  
(d) 168h inhibitor treated sample (2000x)  
(e) EDS mapping of 168h inhibitor treated sample (3000x)  
(f) EDS spectra of mapping 168h inhibitor treated sample

Figure 5.5: SEM images HSS
5.3. Surface analysis

Figure 5.6: EDS point measurements on HSSI samples: Measured points are highlighted with a red circle.

Table 5.3: Composition of the selected areas according to the EDS measurements

<table>
<thead>
<tr>
<th>Point</th>
<th>O (wt%)</th>
<th>Si (wt%)</th>
<th>Fe (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>009 (Reference)</td>
<td>-</td>
<td>0.24±0.14</td>
<td>92.58±0.61</td>
</tr>
<tr>
<td>007 (168h)</td>
<td>0.70±0.06</td>
<td>0.92±0.10</td>
<td>96.68±0.46</td>
</tr>
</tbody>
</table>

Figure 5.7: SEM images of 168h corroded HSS samples
Discussion
The substrates, only immersed in 0.05 M NaCl, clearly reveal corrosion products that cannot be found on the inhibitor treated samples. Only GA steel sometimes reveal localized corrosion products when the inhibitor is applied. These products have been compared to corrosion products which can be found in the inhibition performance over time experiment (see section 4.3.3). It appears that they have the same chemical composition. Perhaps these products are formed due to insufficient sodium silicate in solution. The performance experiment showed that increasing the concentration suppressed the formation of these products. It is known from literature that local corrosion is actually intensified when silicate in solution is insufficient, due to the formation of an incomplete protective layer [146]. Despite these local corrosion products on GA steel, a relatively large surface area is still undeteriorated. This observation clearly demonstrates the protective properties of the inhibitor.

Both substrates did not show any evidence of a silicate layer on SEM images. Perhaps the layer is very thin, evenly spread and follows the topology of the metal surface, which makes it difficult for the equipment to distinguish between a layer and a metal surface. The Langmuir model from section 5.2 already suggested a monolayer at 30 minutes of treatment time, which can be in order of nanometres to micrometres. Several attempts to reveal the layer have been made. For example, it has been tried to vary the acquisition voltage from 15 kV to 0.1 kV. Besides seeing less details due to the lower voltage, only NaCl crystals could be detected. Additionally, setting the imaging mode to backscattered electrons also did not provide any visible information about the existence of a silicate layer. The EDS measurements on the other hand, did indicate an increase of Si and O content, which could suggest a layer being formed. The increase was homogenous, implying a full layer coverage. However, it must me noted that the EDS mappings were made at a magnification of 3000x and lower magnification mappings were not made due time constraints. It is unsure if lower magnification mappings would reveal an inhomogeneous increase of Si and O on the metal surface. Furthermore, the increase is of these elements was not very significant and coupled with the difficulties of the EDS equipment to detect light elements, make the results of the EDS not very reliable. To support the Si and O increase as a result of a layer formation, additional techniques should therefore be consorted. Techniques such as the atomic force microscopy (AFM), transmission electron microscopy (TEM), X-ray reflectivity (XRR) or Auger electron spectroscopy (AES) can possibly reveal the layer. Unfortunately, due to time restrictions, these techniques could not be carried out.

Literature studies concerning the visibility of the silicate layer report various observations depending on the experimental conditions. For example, Gao et al. revealed a transparent film on a magnesium alloy, which becomes more opaque when the sodium silicate concentration is increased [143]. However, the clear structure of the film could not be observed. Furthermore, the conditions were not similar as the condition reported in this report. The pH of their solution was 8.2 and also contained Na₂SO₄ and NaHCO₃. Salasi et al. revealed a porous network of spherical silicates (average size = 0.5 µm) on carbon steel, already visible at a magnification of 500x [144]. However, it must be noted that they adjusted the pH to 8, which is known to cause increased polymerization of silicates leading to the formation of colloids [143, 145]. Furthermore, they used a higher concentration inhibitor, which is also known to increase the degree of polymerization [146]. Dalbin et al. revealed a very thin brittle glassy silicate layer which was smaller than 500 nm in thickness. They observed the layer by tilting the sample and observing the edge of a crack, caused by a scissor cut [147]. It must be noted that Dalbin heated their samples after treatment at temperatures varying between 50 and 200 °C, which can also increase the degree of polymerization of the silicate layer.
Conclusions
The following conclusions have been drawn:

- SEM images of GA substrates treated with sodium silicate reveal a surface that resembles untreated samples, which indicate good protective properties of the inhibitor. However, there are still few indications of local corrosion. SEM images of treated HSS samples show a similar result. The amount of observed localized corrosion is, however less compared to GA steel.

- Neither GA steel nor HSS steel treated with inhibitor showed a visible protective layer on the SEM images. The layer is possibly too thin to be detected.
5.3.2. FTIR measurements

FTIR measurements can reveal which kind of chemical bonds are present on the surface of a sample. By comparing a bare sample with an inhibitor treated sample, FTIR can reveal if there is a layer being formed. The chemical bonds can also provide information how the layer is build-up and thus can provide structural information.

Raw data obtained from FTIR experiments have been baseline corrected and studied. The full spectra for different immersion time intervals (0.5, 2, 4, 8, 24, 48 and 168 hours) can be seen in figure 5.8. A week of exposure was chosen to simulate corrosion of a car during use (i.e. a trip from Amsterdam to Berlin during heavy rainfall). Reproducibility of the peaks for each immersion time can be found in appendix C.1. The spectra for both substrates show similar peaks and three distinct regions can be seen: 4000-3000 cm$^{-1}$, 2000-1400 cm$^{-1}$ and 1400-650 cm$^{-1}$. Besides several clear peaks, it is noticed that some peaks shift per time interval, especially in the lower frequencies.

Both substrates also express the so-called “fringing effect”, which occur above 3000 cm$^{-1}$ and between 1900-1400 cm$^{-1}$. The fringes are characterised by a cosine like wave with equal periods. They originate from e.g. internal reflection of the film, which causes constructive and destructive interference of the IR beam [152]. The fringes can give indication of a smooth surface [153]. Apart from internal reflection, electronic interference (i.e. transient power spikes in power supply) might also lead to fringes. The fringing effects can be used to determine layer thickness of thin films if they have a flat surface [154]. However here, fringing is considered as noise.

4000-3000 cm$^{-1}$ Absorption in this region is typical for O-H stretching vibration and is an indication of the layer containing hydrogen [155]. The peaks in this region do not show a clear change in intensity with increasing time interval. Apart from the fringes, two clear peaks can be seen on both substrates. The peaks at around 3730 cm$^{-1}$ and 3630 cm$^{-1}$ can be assigned to silanol groups, respectively, SiO-H stretch (vicinal or germinal) and SiO-H stretch isolated [62]. Neighbouring silanol groups can form a configuration through hydrogen bonding between H-H and O-H. This is called vicinal or germinal silanols (see figure 5.9b&c). Isolated silanol groups are silanol groups that are separated from each other, disabling their interactions (see figure 5.9a).

2000-1400 cm$^{-1}$ This region is usually characterised by the presence of molecular water at 1650 cm$^{-1}$ or organic carbon double bonds [62, 156]. The spectra in this region shows strong tendency to show fringes, which makes it difficult to assess the difference between actual peaks and noise. Furthermore, peaks tend to fluctuate here in strength and a clear structure could not be observed. HSS seems to show a feint peak around 1400, which is an indication of the presence of Na-OH bonds [157]. In contrast, this peak is not well observed in the GA steel spectra.

1400-650 cm$^{-1}$ This region contains the peaks which are the most pronounced and reveals the presence of vibrational modes of Si-O-Si groups [62, 158, 159]. The strongest and most clear peak can be found between 1300-950 cm$^{-1}$ and can be assigned to asymmetric stretching of Si-O-Si bonds or Si-O-M bonds (M= Fe or Zn) [159, 160]. The peak observed at 1083 cm$^{-1}$ is called the transverse optical 1 (TO1) resonant mode and contains contains a shoulder at the high frequency side around 1200 cm$^{-1}$. A low frequency shoulder is also observed at between 1050 and 1000 cm$^{-1}$, but occurs mostly on the HSS samples. The spectra below 950 cm$^{-1}$ contain information about other Si-O-Si resonant modes [62, 158]. A feint peak can be observed for both substrates around 800 cm$^{-1}$, which can be assigned to symmetric stretching of the Si-O-Si bond [161].

A summary of the assignments of the peaks can be found in table 5.4. It must be noted that many factors can induce peak frequency shift, for example, inhomogeneity, densification, porosity and film thickness. These factors are also interdependent, thus it is not always clear where the peak shifts originate from [151]. Therefore frequencies that are described in literature do not need to correspond exactly and it is sufficient to be in the described frequency range.
Table 5.4: Assignment of the peaks observed in the FTIR spectra

<table>
<thead>
<tr>
<th>Vibrational mode assignment</th>
<th>Frequency</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-O-Si groups</td>
<td>1300-400</td>
<td>[62, 162–164]</td>
</tr>
<tr>
<td>Si-O-Si symmetric stretch</td>
<td>~800</td>
<td>[161]</td>
</tr>
<tr>
<td>Si-O-M (M= Fe or Zn)</td>
<td>1200-950</td>
<td>[160]</td>
</tr>
<tr>
<td>Si-O-Si stretch (TO1)</td>
<td>1085</td>
<td>[62, 158]</td>
</tr>
<tr>
<td>Si-O stretch (TO2)</td>
<td>1200</td>
<td>[165, 166]</td>
</tr>
<tr>
<td>Na-OH</td>
<td>1400</td>
<td>[157]</td>
</tr>
<tr>
<td>Molecular water bending</td>
<td>1650</td>
<td>[62, 164]</td>
</tr>
<tr>
<td>Si-OH</td>
<td>2800 - 3700</td>
<td>[158, 164]</td>
</tr>
<tr>
<td>Si-OH stretch (vicinal or geminal)</td>
<td>~3730</td>
<td>[62]</td>
</tr>
<tr>
<td>Si-OH stretch isolated</td>
<td>~3660</td>
<td>[62]</td>
</tr>
</tbody>
</table>

Figure 5.8: FTIR spectra with grazing element for substrates immersed in 2 g/L sodium metasilicate and 0.05 M NaCl at different time intervals: Dashed lines indicate peaks.
Discussion

The broad peak between 1300-950 cm\(^{-1}\) shows a clear increase or decrease in intensity over time. To follow this behaviour, the surface below this peak was measured and plotted versus time (see figure 5.10). The plot reveals a fluctuating peak intensity over time for both substrates, especially in the short time intervals.

![Figure 5.9: The fundamental stretching vibrations of different hydroxyl groups: (a) non-hydrogen-bonded silanols (isolated groups), (b) hydrogen-bonded silanols (vicinal groups) and (c) hydrogen-bonded silanols (geminal groups), (d) silanol hydrogen-bonded to molecular water, (e) free molecular water. Figure reproduced from Aguiar et al.](image)

![Figure 5.10: Graphical presentation of the Si-O-Si peak intensity versus time: The peak under 1080 cm\(^{-1}\) has been measured and plotted versus time. Explanation of the surface measurement can be found in appendix C.2.](image)

The intensity and broadness of the peaks is related to the amount of chemical bonds present in the sample. Therefore, the results of figure 5.10 can be used as an indication for the relative layer thickness. However, to relate them to absolute values, they need to be calibrated to absolute layer thickness. Kane et al. determined the thickness of a very thin polymer layer with this method by using ATR-FTIR in combination with AFM. The results were promising, but their calculated values still differ 10% from real measured values [167].

During FTIR measurements, it was noticed that peak intensity fluctuated noticeably per measured area on the same substrate. This is reflected in the large error bars in figure 5.10. The large spread might be caused by the fact that the measurement could not be done at the same location and on the same substrate. For each time interval, a fresh sample was used, which might have a slightly different chemical surface. Surface roughness, which causes scattering of the beam can also have an effect. Furthermore, there is also the possibility of layer formation on preferential sites, which grows in time and causes certain areas to have a thicker layer than on other areas. The relative large error implies that hard conclusion cannot be drawn from figure 5.10 when regarding the layer thickness. To accurate measure it, surface sensitive techniques like XPS or ToF-SIMS should be applied. Unfortunately, these measurements could...
not be performed during this research.

The obtained spectra have been compared to several works containing sodium silicate [157, 163, 164]. In these papers, FTIR spectra can be seen that resembles figure 5.11. Comparison to the spectra obtained in this report reveal a clear discrepancy in peak intensity and broadness in the 3800-3000 cm\(^{-1}\) region. This broad peak indicates bonded water with the Si-OH bonds (see figure 5.9d). Instead of one single broad peak, two low intensity peaks are visible in the present study. Furthermore, in literature the characteristic water peak at 1650 cm\(^{-1}\) is often visible, indicating surface absorbed water or water caught in the structure cavities. In this study, this water peak does not appear. The absent of these water related peaks suggest that there is no or little bonded water in the studied sample.

![Figure 5.11: Normalized Infrared spectra for water glass of moduli \(n = 3.35-0.99\) with schematic representations of stretching (peak centered around 3250 cm\(^{-1}\)) and bending (1600 cm\(^{-1}\)) of OH groups. The silicate fingerprint region is found between 800 and 1200 cm\(^{-1}\). Figure reproduced from Jansson et al. [163].](image)

The peaks found in the 1300-400 cm\(^{-1}\) region are often the focus of interest, because the peaks there are in the fingerprint region. This area consist of several absorption bands, which can overlap. Due to the fact that the FTIR equipment can only measure an average of multiple bands, the less dominant overlapping bands can be masked and only the dominant peak and the shoulders are visible (see figure 5.12). The peak centred around 1083 cm\(^{-1}\) found in this study, is perhaps composed of multiple peaks, which is indicated by its broadness and the existence of high and low frequency shoulders [166, 168].

![Figure 5.12: Schematic of the FTIR measurement spanning over several overlapping peaks (black). The measured peak (bold dotted) will only reveal the dominant peak and shoulders. Figure adapted from Fidalgo et al. [161].](image)
The assigned peaks and shoulders from the FTIR spectra, highly suggest the formation of a silicate layer which consists of polymerised tetrahedral silicates; SiO$_4^{4-}$ (see figure 5.16a). The degree of polymerisation will determine the structure of the layer. Low order polymerisation will generally create a thin adsorbed layer, whereas higher order polymerisation will create colloids, gels, etc. (see figure 5.14).

There are many parameters which determine the order of polymerisation, which also interdepend on each other, such as the SiO$_2$:Na$_2$O ratio, the pH of the solution, the concentration, etc. The SiO$_2$:Na$_2$O ratio gives the proportion of silica to alkali in a sodium silicates. Ratios below 1 will generate monomeric species, while higher ratios will produce more polymeric species [157, 162].

The pH is an important factor, as it is known that low pH will promote polymerisation, while high pH will promote depolymerisation. The effect of the pH and concentration can be graphically presented in figure 5.13. Here, 3 zones exists:

- Zone I: The monomeric region, containing monomeric species (i.e. Si(OH)$_4$, Si(OH)$_3^-$, SiO$_2$(OH)$_2^{2-}$)
- Zone II: The stable polymeric region, containing silicate polymers
- Zone III: The insolubility region, containing amorphous silica precipitates

![Figure 5.13: Species in equilibrium with amorphous silica. Diagram computed from equilibrium constants (250°C). The line surrounding the shaded area gives the maximum soluble silica. The mononuclear wall represents the lower concentration limit, below which multinuclear silica species area not stable. In natural waters the dissolved silica is present as monomeric silicic acid. Note: this diagram shows the general behaviour of silicates, factors such as time and the SiO$_2$:Na$_2$O ratio are also needed to be taken into account. Figure reproduced from Asrar et al. [161].](image)

Slight variations in the parameters can drastically change the structure of the silicate layer. These factors and many other therefore make it difficult to predict what the degree of polymerisation will be. However, several papers have studied the vibrational bands of Si-O-Si bonds in the 1300-400 cm$^{-1}$ region and have assigned them to the degree of polymerization of SiO$_4^{4-}$ expressed in Q$^n$-units. Here, Q stands for quaternary (tetrahedron SiO$_4^{4-}$) and $n$ denotes the number of bridging oxygens [169]. The value $n$ can have values between 0 and 4, with 0 for monomeric species and higher numbers for more polymerised species (see figure 5.16b).
The intense peak at 1083 cm\(^{-1}\) can be assigned to a \(Q^3\) connectivity, whereas the shoulder of 1200 cm\(^{-1}\) can be assigned to \(Q^4\). The shoulder at 1050 cm\(^{-1}\) is assigned to \(Q^2\) species. The assignments of the peaks thus suggest the silicate layer consisting mainly of trimers with traces of tetrameric and dimeric species. A paper published by Nordstrom et al. showed similar assignment [170]. Albeit with a SiO\(_2\) and KOH mixture, Simonsen et al. also showed a similar assignment of peaks to the \(Q^9\) connectivity [145].

As already mentioned, peak shifts could be observed in the spectra per time interval in this report. Shifts towards higher frequencies indicate a transformation towards higher degree of polymerisation, while shifts in the lower frequencies imply depolymerisation to lower order silicate polymers [145, 171]. To assess the peak shifts, the spectra per time interval have been compared (see appendix C.1). It appears that for GA steel, in time the 1200 cm\(^{-1}\) shoulder moves more to lower frequencies and the peaks at 3730 and 3630 cm\(^{-1}\) become less evident. Peaks in the low frequency appear to disappear gradually. In retrospect, the HSS samples do not reveal a clear shift in the peaks. Instead, the peaks tend to fluctuate in strength per time interval.

The observation leads to the conclusion that the silicate layers of GA steel and HSS are different. GA steels have a layer consisting of mainly trimers and tetramers which obtains a more trimeric character over time. HSS has a layer consisting of tetra-, tri-, di-, and monomeric species. As time evolves, the species vary by polymerisation and depolymerisation. This evolution might be due to an aging process. According to several works, sodium silicate solutions can age over time: polymerisation and depolymerisation can occur in time depending on multiple factors [172, 173]. pH measurements were carried out during the FTIR experiments. After immersion, the used solution was measured and results are summarised in figure 5.15. A clear difference in pH evolution can be seen between the reference and the inhibitor solutions. The steady decrease in pH can be related to the aging process. Any depletion of the silicate ions, caused by polymerisation, adsorption or complexing with surface oxide film can cause a pH drop [173]. The pH drop supports the hypothesis of the possible aging of the layer.

The difference in polymeric species might affect the density or compactness of the layer. According to Yuan et al., a higher degree of polymerisation will often result in a more compact layer [157]. Whereas a layer consisting of mono- and dimeric species will be less dense, since these species have more free bonds which water can form H-bonds with. This will result in a layer that is less homogeneous and therefore less dense. In other words, perhaps the layer of GA steel is denser than that of HSS and therefore might express a different corrosion inhibition behaviour. However, additional experiments are required to proof this, as the \(Q^n\) connectivity only suggest a degree of polymerisation and not the real structure. Ring structures and other more complex structures can also be formed [175] and they can also determine the compactness of the layer. Generally, FTIR measurements of silicates are performed in junction with other structural determination techniques such as \(^{29}\)Si-NMR and Raman spectroscopy [157, 162, 163]. The cause of the different degrees in polymerisation of the layers has not been reported in literature to the knowledge of the author. The used inhibitor solutions are identical for both substrates, only the substrates are different. Perhaps, different surface chemistries per substrates influence the polymerisation of the silicates. The different adsorption activation energy obtained in section 5.2 might imply this.
Figure 5.14: Polymerisation behavior of silicates. Figure reproduced from Ralph K. Iler [174].

Figure 5.15: pH evolution of the samples during immersion
(a) Structure of tetrahedral silicate (SiO$_4^{4-}$)

(b) A summary of the structure of $Q^0$ to $Q^4$. Figure reproduced from Yuan et al. [157].

Figure 5.16: Possible structures found with FTIR

It must be emphasized that the samples were dried naturally in a desiccator prior to FTIR analysis. The liquid film that dried on top of the substrate in the desiccator therefore will have an increased concentration of silicates. It is known that increasing the concentration, increases the degree of polymerisation. However, the effect might be minor, as the liquid film was thin and evaporation was fast (≈5 min.), which might prevent continued polymerisation. Additionally, due to equipment sensitivity issues, spectra below 650 cm$^{-1}$ were not made. They do however, contain additional Si-O-Si bond information. These considerations should be kept in mind regarding the FTIR conclusions.

Conclusions
The following conclusions have been drawn:

- Treatment with sodium silicates resolves into the formation of a silicate layer.
- The silicate layer of GA steel contains mainly tetra- and trimeric silicate species which age over time to more trimeric species at the expense of the tetrameric species.
- The silicate layer of HSS contains a variety of silicate species ranging from monomeric to tetrameric species from which the amount fluctuates over time.
5.4. Electrochemical analysis

5.4.1. LSV measurements

Additional polarisation measurements were made to understand the nature of the inhibition mechanism of sodium metasilicate; is the inhibitor anodic/cathodic/mixed? Additionally, LSV measurements can also help determine if the alkalinity of sodium metasilicate plays a role in the inhibition.

The polarisation curves for sodium metasilicate are plotted in figure 5.17.

![Figure 5.17: Polarisation curves of sodium metasilicate at different concentrations: All solutions contained 0.05 M NaCl. Here, 0 g/L indicates the reference sample without inhibitor.](image)
GA steel

**Reference sample**  The reference measurement for GA steel gave an $E_{\text{corr}}$ of around -0.55 V vs SHE. The anodic curve represents the dissolution of zinc and is activation controlled up to -0.40 V vs SHE. It must be noticed that the Tafel slope is quite low, indicating that the dissolution of zinc was very active and that corrosion was limited by oxygen. Initially, tests were done with higher concentrations of NaCl (0.1 M and 0.6 M). The higher concentrations gave almost a horizontal Tafel slope (<50 mV/dec) and were too aggressive to give good LSV results.

At high potentials, around +0.75 V vs SHE (not shown in figures), a very small passivation region can be found. This passivity is quickly broken up and thus indicates that the corrosion products of zinc do not form a very good protecting layer.

The cathodic curve represents reduction reactions and reveals a diffusion controlled region starting from -0.6 V vs SHE and lower. Here, oxygen reduction takes place:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad (5.11)$$

At a potential of around -1 V vs SHE, water reduction takes place:

$$2H_2O + 2e^- \rightarrow H_2(g) + 2OH^- \quad (5.12)$$

This is not shown in the graph, but is also characterised by a change in curvature.

**Inhibited samples**  Sodium metasilicate appears to be an anodic inhibitor, indicated by the positive potential shifts and lower corrosion current densities. A passive region can be noticed at a concentration of 2 g/L and 5 g/L. This might be an indication of a passive layer that was formed on top of the substrate. This passive region is abruptly diminished at a -0.1 V vs SHE, probably due to break down of the layer. The 5 g/L concentration did not show a breakdown potential, but it might at higher potentials. The lower concentrations did not seem to show passivity. At low concentrations, the cathodic tail is largely affected by oxygen diffusion, whereas at higher inhibitor concentrations this effect is reduced more and more. This observations leads to the conclusion that increasing levels of sodium silicates lowers the corrosion activity.

HSS

**Reference sample**  The reference measurement for HSS gave an $E_{\text{corr}}$ around -0.3 V vs SHE, which indicates that HSS is nobler that GA steel. However, it does have a higher corrosion current density, implying that HSS corrodes faster. This can be attributed to the fact that the corrosion products of GA steel, zinc oxide, inhibits its own reaction and therefore corrodes slower [178].

The anodic curve represents the dissolution of steel and is activation controlled up to 0 V vs SHE. In contrast to GA steel, the anodic Tafel slope of HSS showed a larger slope than for GA steel. Corrosion activity of HSS was less limited by oxygen, therefore corrosion of HSS was under mixed control. Oxygen diffusion control starts around -0.4 V vs SHE, whereas water reduction starts at -0.75 V vs SHE (not shown).

**Inhibited samples**  Like GA steel, increasing the concentration of metasilicate seemed to shift the curve towards noble values and lower corrosion current densities for HSS. This implies that sodium metasilicate is also an anodic behaviour on HSS. The anodic curves of 2 g/L and 5 g/L exhibited a passive region, just as with GA steel. The breakdown potential was not observed, due to the measurement boundaries that were set up. However, it might be observed at higher potentials. The cathodic curves seem to shift to more activation control with increasing concentration.
Discussion
To confirm the nature of the corrosion inhibition (anodic, cathodic or mixed inhibition), the anodic and cathodic branch were both swept separately starting ±50 mV from the OCP. Plots can be found in figure 5.18. The separate polarization sweeps reduces surface modification and therefore a more accurate representation of the data.
From the plots a large anodic shift can be observed accompanied with lower corrosion current densities. This confirms the observations of the initial LSV measurements: sodium silicate is an anodic inhibitor. Literature studies with sodium silicate support this behaviour [125, 143, 179]. The consensus is that the silicate ions are negatively charged and will migrate to the positively charged anodic sites [137, 138].

Knowing that sodium silicate is an anodic inhibitor, one would have expected to see preferential sites on EDS mappings (see section 5.3). However, the mappings showed the opposite: a homogeneous increase in silicate. The cause of this might be since mappings were made after one week of exposure to the inhibitor. Perhaps, localised Si and O deposits can be revealed at shorter treatment time, but these short time EDS mappings were not made due to time restrictions. According to Asrar et al. the negative charged silicates will indeed migrate towards the positive charged anodic sites. There, they will react with the metallic cations to form a protecting layer. However, it appears that with a continuous feed (excess amount of silicates still present in the solution), the film will extend itself to the cathodic sites and eventually cover the whole substrate [146, 148]. Unfortunately, the paper did not discuss the exact cause for the cathodic extension, nor did it discuss the kinetics of this coverage.
In literature, it is known that second phase particles or even grains of the matrix with a slight different chemical composition can behave anodically or cathodically towards the matrix. The particles or grains can even exhibit a changing galvanic polarity when the corrosion process ensues [149, 150]. In the present study, it is possible that initially the anodic area is fully covered by a silicate layer in a short timescale. When the anodic surface is fully covered, the uncovered cathodic sites might change its polarity, becoming anodes. These new anodes can be covered by the inhibitor as well, thus eventually covering the whole surface area. Of course, additional experiments are required to prove this, such as SVET measurements, which can visualize and follow the ionic currents during the corrosion process. An alternative would be the execution of the LSV measurements of the substrates after one week of exposure to the inhibitor solution and observing the shift in polarisation.

As already was mentioned in chapter 4, the 2 g/L sodium metasilicate solution was alkaline (pH≈12.3). By using the $E_{corr}$ values for the corresponding substrate and the pH value, the Pourbaix diagrams (see appendix A.2) can predict the stability metal. At $E_{corr}$=−0.3 V, GA steel appear to be in the stable range. At $E_{corr}$=−0.1 V, HSS is also in the stable range. It is possible that corrosion activity of the substrates is lowered due to it being in the passivation state caused by the alkaline environment and not due to the formation of a layer by the inhibitor. In other words, it is possible that sodium metasilicate is a pH buffering inhibitor. Some papers have also argued the effectiveness of the layer of sodium metasilicate [176], due to the fact that reports about this topic are quite conflicting.
To test if the inhibition by sodium metasilicate is due to the change in pH, a reference solution of 0.05 M NaCl was adjusted with NaOH to pH≈12.3 (same as the pH of 2 g/L metasilicate). Both substrates were subjected to the alkaline reference solution under the same conditions as the sodium metasilicate solution and were measured. It was expected that if sodium metasilicate acts as a pH buffer, the curves would not significant differ from the 2 g/L sodium metasilicate curves. The results are plotted in figure 5.19 and summarised in table 5.5.
5.4. Electrochemical analysis

Figure 5.18: Separate polarisation sweeps starting ±50 mV from the OCP to determine the inhibition nature of sodium silicate: The reference contained 0 g/L inhibitor. The test solutions had a concentration of 2 g/L inhibitor.
Figure 5.19: Comparison of inhibition of HSS by 2 g/L sodium metasilicate (pH = 12.3) and 0.05 M NaCl with pH adjusted with NaOH to = 12: It can be clearly seen that the graphs are very similar, except for noise and a slight potential shift.
Table 5.5: LSV pH

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$E_{corr}$</th>
<th>$b_a$</th>
<th>$b_c$</th>
<th>$i_{corr}$</th>
<th>$\eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>GA steel - Reference</td>
<td>-552</td>
<td>94</td>
<td>-318</td>
<td>10.7</td>
<td>-</td>
</tr>
<tr>
<td>GA steel - Inhibitor</td>
<td>-332</td>
<td>536</td>
<td>-386</td>
<td>0.5</td>
<td>96</td>
</tr>
<tr>
<td>GA steel - Reference at pH ≈ 12.3</td>
<td>-896</td>
<td>8262</td>
<td>-341</td>
<td>40</td>
<td>-237</td>
</tr>
<tr>
<td>HSS - Reference</td>
<td>-337</td>
<td>367</td>
<td>-661</td>
<td>24.9</td>
<td>-</td>
</tr>
<tr>
<td>HSS - Inhibitor</td>
<td>-130</td>
<td>832</td>
<td>-145</td>
<td>0.5</td>
<td>98</td>
</tr>
<tr>
<td>HSS - Reference at pH ≈ 12.3</td>
<td>-55</td>
<td>1468</td>
<td>-448</td>
<td>3.7</td>
<td>85</td>
</tr>
</tbody>
</table>

The results clearly demonstrate that the inhibition mechanism is not solely due to the change in pH. The alkaline environment certainly affects the curve, as the $E_{corr}$ and the $i_{corr}$ have been altered. However, the increased pH still underperforms compared to the inhibitor, which provides a higher passivation with lower corrosion current densities. Furthermore, the curves do not resemble the inhibitor sample curves for both substrates. It may therefore be concluded that sodium silicate is not a pH buffering inhibitor and that the protection mechanism is mainly due to the formation of a protecting silicate layer. Lahodny-Sar et al. also questioned the effect of silicate and pH and conducted several tests. They measured polarisation curves with different silicate concentrations on steel and varying pH and compared them with normal tap water at the same pH. From those experiments, they concluded that corrosion inhibition is largely due to sodium silicate itself and not due to the alkalinity [179].

Conclusions
The following conclusions have been drawn:

- Polarisation of the substrates with inhibitor showed the occurrence of passivity, which indicates the formation of a protecting layer.

- Separate polarisation sweeps for the anodic and cathodic branch showed an increase of the corrosion potential for both substrates as well as a decrease in the corrosion current density. Therefore, sodium metasilicate is an anodic inhibitor.

- For both substrates, polarisation under alkaline conditions showed lower passivation and higher corrosion current densities than polarisations with inhibitor. Therefore, sodium metasilicate is not a pH buffering inhibitor. The protection mechanism is mainly due to the formation of a protecting layer.
5.4.2. EIS measurements

Impedance measurements can provide information about the corrosion activity during longer periods. The data can also be fitted to models, which can give a physical interpretation.

Impedance measurements were carried on both substrates to see the corrosion evolution in time in presence of the inhibitor and without. The substrates were exposed to the inhibitor solution (2 g/L + 0.05 M NaCl) and the reference solution (0.05 NaCl solution) for one week. The intervals were the same as for the FTIR experiments (0.5, 2, 4, 8, 24, 48 and 168 hours). The Nyquist and Bode plot of the impedance measurement can be found in figure 5.20 for GA steel and in figure 5.21 for HSS.

GA steel  The Nyquist plot for the inhibitor samples reveal a part of a semi-circle, which increases and decreases in radius with time. Comparing the inhibitor samples to the reference, reveal a great difference in capacitance; almost a factor 100. Furthermore, the semi-circle of the reference is more pronounced and the full arc tends to be more visible with elapsing time (not shown). The reference arcs also reveal, at short time intervals (0.5 and 2 hours), an induction loop. In the low frequency range (right part of arc), there are indications of a second time constant. However, they do not appear in the Bode plots. In the high frequency range (left part of the arc), a feint semi-circle with a negligible arc radius can be detected for all time intervals.

The Bode plot for the inhibitor samples reveal an almost linear behaviour in the low and mid-range frequencies. Small shifts (range of ≈100 Ω cm²) in the Z-modulus occur as time elapses. The reference samples reveal a very different behaviour. Here, linear behaviour can be observed mostly in the mid-range frequencies after which a plateau is reached in the low frequencies. Furthermore, a clear decrease in Z-modulus mostly affects the mid-range frequencies with increasing time, except for the 168h time interval.

One single broad peak can be found in the phase-angle Bode plots for both the inhibitor sample and the reference, which corresponds to one time constant. The theta angle shift for both samples do not initially differ significantly, but after 48h, the shift becomes noticeable. The phase angle does not seem to be shifted much in frequency for the inhibitor samples and the time constant fluctuates around 1 Hz. In contrast, the reference sample largely shift towards lower frequencies with passing time. After 24h, the shift seems to halt, as the time constant fluctuates around 0.5 Hz and the theta angle decreases.

HSS  Similar to the GA steel, HSS samples immersed in inhibitor solution reveal part of a semi-circle. Here, a clear decrease in capacitance can be observed with increasing time. The capacitance loop of the reference samples show an almost full semi-circle, which is almost a factor 100 smaller than the inhibitor samples. GA steel likewise, the short time intervals shows an induction loop. The capacitance loop of the reference sample does not reveal a clear decrease in capacitance. At the high frequency side of the Nyquist plot, a feint indication of a second semi-circle can also be detected with the HSS reference (see figure 5.22). Similar to GA steel, this semi-circle is almost negligible and is not revealed in the Bode plots.

The Bode plot for the inhibitor samples also point out a linear behaviour for the low and mid-range frequencies. Small variation in Z-modulus occur, but a decrease becomes evident after 48h. The decrease affects both the small and the mid-range frequencies. Except for the 2h interval, the reference samples show a small decrease or increase in Z-modulus which also affect both the small and the mid-range frequencies. The reference also exhibit a plateau at the lower frequencies.

Similar to GA steel, 1 time constant is observed for both samples in the phase angle Bode plot. The phase angle of the inhibitor treated samples initially shift towards higher frequencies with elapsing time, after which a decrease is observed starting from 48 hours. The time constant also decreases in phase angle relatively largely after 48 hours compared to the initial time intervals. For the reference samples, the time constant fluctuates both in frequencies as well as phase angle around 0.3 Hz and -35°.
Figure 5.20: Impedance plots for GA steel
Discussion

The almost linear behaviour of the inhibitor samples can be related to a purely capacitive behaviour, which characterises an effective barrier [180]. The reference samples on the other hand, reveal a Z-modulus plateau which can be related to an imperfect coating. Here, the linear part still reflects the capacitive behaviour, while the plateau reflects charge transfer resistance of the corrosion layer [53].

The induction loops in the low frequencies found for the reference samples of GA steel and HSS have been reported in literature [17]. They generally tend to occur in near neutral solution and several explanations exists for this phenomena. The most accepted one is attributed to the relaxation processes of the adhesion of inactive metallic ions on the surface resulting from the corrosion process [181–183].

The occurrence of the induction loops seem to only appear for the short treatment time (<2h), when the system was probably not yet stable. Deviation from a semi-circle behaviour in the low frequency domain expressed in the GA steel reference samples have been observed by Da Silva et al. with GA steel at a 0.01 M NaCl [17]. According to them, these effects can be associated dissolution of residual zinc.

A parameter which can be easily used to compare the corrosion resistance of different samples is the Z-modulus in the low frequency range. The low frequencies are related to the corrosion activity at the interphase of the metal/layer [184]. Larger Z-moduli imply better corrosion protection performance [143]. The great difference in Z-moduli of the inhibitor treated samples and the reference samples clearly demonstrate the inhibiting effect of sodium metasilicate.

It must be noted that the Z-modulus plotted in figures 5.20 and 5.21 is the total Z-modulus, which is build-up of multiple moduli (such as $Z_{\text{solution}}$, $Z_{\text{doublelayer}}$, etc.) However, in the lower frequency range, the moduli of the metal/layer interphase dominate.

For all samples, the decrease in Z-modulus in the low frequency range can be attributed to water molecules and active chloride ions penetrating the protective layer [143]. The increase can be related to the build-up/restoration of the protecting layer. For the inhibited samples, the fluctuation in Z-moduli seems to be small indicating a stable protective layer. However, its effectiveness gradually decreases after 48h. For HSS, this effect seems to be stronger than for GA steel. Still, the inhibited samples always show higher Z-moduli compared to the reference samples, thus proving furthermore the inhibitor effectiveness as time elapses.

The Z-moduli at 0.01 Hz for the inhibited samples have been plotted versus time in figure 5.23. The HSS samples reveal a decrease in time, which is generally observed in studies concerning coatings and can be attributed to penetrating water molecules and chlorides [185]. The GA steel samples, in contrast, seem to reveal a peak in the Z-modulus after which a recovery takes place after 48 hours. To the knowledge of the author, this is behaviour has not been well documented in literature. Perhaps this phenomenon can be linked to the density of the protective silicate layer. Reflecting on the results of the FTIR experiments, it was discussed that the silicate layer of GA steel was perhaps denser than that of HSS and
that aging occurs. It is possible that the dense layer of GA steel reached its maximum density around 24 hours and after that became instable, depolymerised partly and became less dense. The layer might have slowly recovered afterwards, as from literature it is known silicate layers can recover their protective properties after sustaining damaging if sufficient silicates remain in solution after the initial film forming [146, 176]. The HSS layer on the other hand, might have a too open structure that does allow protection, but keeps weakening in time due to increased permeability of ions.

Figure 5.23: Evolution of the $|Z|$-moduli at 0.01 Hz in time: measurement was done in trifold and red line indicates the average of the trifold.
To obtain a more quantitative interpretation of the EIS measurements, the EIS spectra were fitted using appropriate equivalent circuits. The inhibitor EIS spectra in this study showed one semi-circle with one time constant, which highly suggests a Randles behaviour [53]. Therefore, an initial fitting was made with this model and the equivalent circuit is represented in figure 5.24. Besides the small deviations in the high frequency and low frequency range, the spectra of the reference samples also resembled Randles behaviour and therefore this model was also applied for these samples. Fitting data can be found in tables 5.6 and 5.7. The fitting gave percentage errors between 4.5% and 0.5% and chi-squared error magnitudes below 0.002, which imply an acceptable model fit. In this equivalence circuit 3 elements are present:

- \( R_s \), the resistance of the electrolyte
- \( CPE_{film} \), the constant phase element of the film
- \( R_{ct} \), the charge transfer resistance of the film

Instead of a capacitor, it was chosen to represent the capacitive behaviour of the film by a constant phase element (CPE). This is due to the fact that a CPE takes into account the electrode heterogeneity. The impedance function of the CPE is represented as:

\[
Q_{CPE} = \frac{1}{Y_0(j\omega)^{-\alpha}}
\]

(5.13)

where \( Y_0 \) is the capacitance, \( j^2 \) is the imaginary number, \( \omega \) is the angular frequency and \( \alpha \) is the CPE exponent. The latter expresses the heterogeneity of the CPE; \( \alpha \) can have a value between 0 and 1. The case \( \alpha=1 \) describes an ideal capacitor, while \( \alpha=0 \) describes a pure resistor.

![Figure 5.24: Equivalent circuit used for fitting of the EIS response for both substrates.](image)

---

1 According to Ir. M. Meeusen, fittings are appropriate if the percentage error is smaller than 10% and has a chi-square smaller than \( 10^{-3} \).
**Table 5.6:** Fitted impedance parameters for GA steel immersed in inhibitor solution (2 g/L Na₂SiO₃ + 0.05 M NaCl) and without inhibitor (0.05 NaCl)

<table>
<thead>
<tr>
<th>Immersion time (h)</th>
<th>Inhibitor</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rₛ (Ω·cm²)</td>
<td>CPEₚfilm (Ω⁻¹·cm⁻²·s⁻α)</td>
</tr>
<tr>
<td>0.5</td>
<td>213</td>
<td>3.2·10⁻⁵</td>
</tr>
<tr>
<td>2</td>
<td>215</td>
<td>3.8·10⁻⁵</td>
</tr>
<tr>
<td>4</td>
<td>217</td>
<td>3.9·10⁻⁵</td>
</tr>
<tr>
<td>8</td>
<td>222</td>
<td>4.0·10⁻⁵</td>
</tr>
<tr>
<td>24</td>
<td>230</td>
<td>4.7·10⁻⁵</td>
</tr>
<tr>
<td>48</td>
<td>244</td>
<td>6.7·10⁻⁵</td>
</tr>
<tr>
<td>168</td>
<td>226</td>
<td>5.5·10⁻⁵</td>
</tr>
</tbody>
</table>

**Table 5.7:** Fitted impedance parameters for HSS immersed in inhibitor solution (2 g/L Na₂SiO₃ + 0.05 M NaCl) and without inhibitor (0.05 NaCl)

<table>
<thead>
<tr>
<th>Immersion time (h)</th>
<th>Inhibitor</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rₛ (Ω·cm²)</td>
<td>CPEₚfilm (Ω⁻¹·cm⁻²·s⁻α)</td>
</tr>
<tr>
<td>0.5</td>
<td>223</td>
<td>1.1·10⁻⁴</td>
</tr>
<tr>
<td>2</td>
<td>226</td>
<td>1.1·10⁻⁴</td>
</tr>
<tr>
<td>4</td>
<td>228</td>
<td>1.2·10⁻⁴</td>
</tr>
<tr>
<td>8</td>
<td>232</td>
<td>1.3·10⁻⁴</td>
</tr>
<tr>
<td>24</td>
<td>253</td>
<td>1.3·10⁻⁴</td>
</tr>
<tr>
<td>48</td>
<td>269</td>
<td>2.8·10⁻⁴</td>
</tr>
<tr>
<td>168</td>
<td>254</td>
<td>4.9·10⁻⁴</td>
</tr>
</tbody>
</table>

The solution resistance of 0.05 M NaCl solution reported in literature [186–188] showed values in the range of 10 to 50 Ω·cm². There is a large discrepancy between the obtained values and the literature values, which cannot be yet explained.

For both substrates, the α exponent clearly shows a deviation from the ideal capacitor, implying the weakening corrosion protection when time elapses. Only the HSS reference sample shows a stable α value. The other samples show a clear decrease as time progresses.

It is clear that for both samples, the charge transfer resistance of the inhibitor treated samples is an order of 100 times larger than that of the references. The charge transfer resistance can be related to the amount of water and chlorides penetrating the protective layer. More penetration of these molecules means easier charge transfer, thus a lower resistance. The Rₑt values are in agreement with the work of Gao et al., who have investigated sodium silicate on a magnesium alloy and obtained values in the same magnitude [143].

The charge transfer resistance follows the same trend as observed with the Z-moduli at 0.01 Hz (see figure 5.25). From the FTIR results in section 5.3.2, differences in polymeric species in the formed silicate layers was observed. This led to the discussion that perhaps the GA steel layer would be more compact compared to the HSS layer. Related to that, there was also the discussion about the aging process of the layer in time and the possibility of recovery of the layer if the silicate feed from solution was still sufficient. The results from the Randles fitting support the hypothesis made in that discussion. The difference in Rₑt values between GA steel and HSS can be explained by the compactness of the layer. Less dense layers allow better permeability of ions, thus lower Rₑt values. An increase in Rₑt values can be related to the recovery and aging process of the layer. Although GA steel will obtain a layer that will mostly consist of trimers in time and thus becomes more open in time, there is still an increase in Rₑt. Besides aging of the layer, this phenomenon cannot be yet explained. HSS on the other hand, has a layer that is constantly changing, but effectively will still have the same amount of variety of polymeric species. Perhaps here, the recovery and aging process is counterbalanced after 48h by permeability and therefore a constant Rₑt is observed.
In section 5.4.1 it was mentioned that EDS measurements suggested a homogenous increase of Si and O elements on the metal surface, implying that the layer initially was deposited on the anodic sites after which they expanded towards the cathodic sites. Therefore, the silicate might cover the whole metallic surface. These results were not very reliable and additional experiments had to be conducted to prove this. The EIS measurements support the idea of a single layer spanning the whole surface, as the Randles circuit seems the most appropriate fitting. If the silicate layer was partially blocking, it was expected to observe this in the impedance plots. Multiple time constants or deviation from the semi-circle behaviour should then have been occurring. Besides the Randles model, also other models have been fitted (not shown), such as the porous layer model or the partially blocking layer. However, these models gave very large errors, implying that they do not correctly describe the system.

Figure 5.25: Evolution of the $R_{ct}$ values

Conclusions
The following conclusions have been drawn:

- EIS spectra of both substrates show a high Z-modulus in the low frequency range compared to the reference samples. Furthermore this Z-modulus shows a small decrease after 1 week of immersion in inhibitor solution. For GA steel this decrease is smaller than for HSS steel. These observations demonstrate the effective inhibition of sodium silicate, even after a week.

- By fitting the EIS spectra to an equivalent circuit, it was found that the inhibition of sodium silicates is best described by the Randles model. This implies that the metal is covered by a layer of silicates, which protects the metal from corrosion.

- From the Randles model, the charge transfer resistance of the protective layer was determined. The values showed that the layer on GA steel provides better protection compared to the layer on HSS steel. This difference might be due to the difference in permeability of the layers, caused by the difference in polymeric species present in the layers.
5.5. Proposed inhibition mechanism

From the results of the surface analysis, adsorption model and electrochemical analysis of the inhibitor behaviour on both substrates the following inhibition mechanism can be proposed:

Initially, a protective silicate layer will cover the anodic areas of the metal substrates, according to LSV experiments. The Langmuir adsorption isotherm predicts that this initial layer will be a monolayer that will spontaneously form. The isotherm also suggests that silicates from solution adsorpt to the metal substrate by a combination of physisorption and chemisorption. According to the calculated thermodynamic parameters, the silicates will be stronger adsorbed to GA steel than to HSS.

![Diagram of silicate layer on GA steel and HSS](image1)

Figure 5.26: Proposed mechanism: A silicate layer is initially formed on top of the anodic sites

As time elapses, the silicate layer will probably also cover the cathodic areas and a uniform layer will be formed after one week, suggested by EDS, EIS measurements. SEM equipment cannot reveal this layer, as the layer is expected to be very thin, in the order range of nanometres according to literature. Indicated by FTIR, the silicate layer will consist of silicate species with a variety in degree of polymerization, which appear to evolve in time. Initially, the GA steel layer will consist of mainly $Q^3$ and $Q^4$ silicate species, but will gradually shift towards more $Q^3$ species at the expense of $Q^4$ species. In contrast, the HSS layer will contain $Q^3$ to $Q^4$ species and the amount will vary in time, although not significantly. This layer will probably have a more open structure than the GA steel layer due to it containing less polymerized species.

![Diagram of silicate layer on GA steel and HSS](image2)

Figure 5.27: Proposed mechanism: The layer will gradually cover the whole surface. The layer will differ in polymerization composition per substrate

The difference in polymeric species might result in different protective capabilities of the layer against corrosion. Due to its less dense structure, the silicate layer of HSS allows more permeability of ions that can increase corrosion activity. These findings are supported by EIS measurements. Therefore, sodium silicate will be more effective on GA steel than on HSS.

![Diagram of silicate layer on GA steel and HSS](image3)

Figure 5.28: Proposed mechanism: In time, water and chlorides penetrate the silicate layer, lowering its protective properties
Conclusions

The aim of this research was to find an effective inhibitor for galvannealed steel and high-strength steel. To reach this goal, an inhibitor screening was performed. After reviewing the literature, several criteria were applied to compose a list of 30 inhibitors. This list was narrowed down to 7 inhibitors by applying additional selection criteria, such as price and REACH. The selected inhibitors were subjected to an electrochemical evaluation. This was done with LSV experiments to obtain corrosion current densities. Those values were used to calculate inhibitor efficiencies, which were used to compare inhibitors with each other. It turns out that sodium metasilicate and sodium molybdate were two very potent candidates as they yielded 80 to 99% inhibition for both metallic substrates. After an inhibition performance experiment spanning 8 weeks, inhibition by sodium silicate showed little visible corrosion compared to sodium molybdate. Therefore, it became evident that sodium metasilicate was the better inhibitor for GA steel and HSS. A concentration of 2 g/L sodium silicate showed an inhibition efficiency of 96% for GA steel and 98% for HSS when immersed in 0.05 M NaCl solution. Coupled with its low pricing and availability, sodium silicate is the preferred inhibitor.

To understand how sodium metasilicate inhibits the substrates, investigation of the inhibitor mechanism was performed by combining surface analysis, adsorption models and electrochemical analysis. Adsorption models suggested that sodium silicate obeys a Langmuir isotherm, which predicts a spontaneous monolayer. Polarisation experiments showed an increase of corrosion potential coupled with a decrease in corrosion current density, implying an anodic behaviour. Therefore, the inhibitor will initially cover the anodic areas of the metal substrate. As time progresses, the covered area will also span the cathodic areas. This was suggested by EDS measurements, which showed an increase of Si and O content of around 1% across the whole surface. EIS measurements also support a single layer spanning the whole surface, as a Randles fit was most appropriate. This implied the metallic surface being fully covered by a single layer. The formed layer is expected to be very thin, in orders of nanometres, as SEM could not visualize the layer. FTIR analysis revealed that the layer consists of silicate species with various polymeric degrees. GA steel consist of mainly $Q^3$ and $Q^4$ silicate species, but gradually shift towards more $Q^3$ species at the expense of $Q^4$ species. The HSS layer will contain $Q^1$ to $Q^3$ species and the amount will vary in time, although not significantly. The differences in polymeric species affects the structure of the silicate layer, as the GA steel layer will probably be denser than the HSS layer. The structure or compactness can be related to the permeability to ions and therefore the effectiveness of the layer against corrosion. This is supported by impedance measurements, as the GA steel layer with its denser structure gave a 100-fold higher charger transfer resistance than the open structure layer of HSS.

Overall, sodium silicate provides excellent inhibition of galvannealed steel and high-strength steel under the conditions proposed in this report. Hopefully, this inhibitor will also provide fruitful results when it will be applied in future smart coatings for automotive application.
Recommendations

The following recommendations are related to the inhibitor screening selection:

- A selection based on weight-loss measurements could have been applied, instead of LSV. This is a faster and more efficient way. After the weight loss measurement, electrochemical tests should be made to confirm the results.
- A multi-channel array can be substituted for the weight loss measurements to determine the optimal concentration. This might increase speed and efficiency.
- Caffeine was left out, due to the lack of time. It might be interesting to investigate its inhibition still.

The following recommendations are related to the further understanding of the protective mechanism of sodium metasilicate:

- The Stern-Geary equation & cyclic voltammetry should be performed to get more accurate polarization data.
- A study with cyclic polarization should be performed to study the possible repassivation of the silicate layer.
- The silicate layer should be studied with FTIR in situ instead of ex situ.
- Impedance measurements should last for a longer period, especially to test the corrosion resistance of HSS in inhibitor solution.
- The layer thickness should be measured with XPS, TEM of AFM.
- Additional silicate layer structure measurements should be performed with $^{29}$Si-NMR and Raman spectroscopy.
- The inhibitor should be tested under different temperature and NaCl concentrations.

The following recommendations are related to the implementation of the inhibitor into the smart coating:

- A study should be performed to see if the silicate layer can be tailored in compactness, to improve water permeability resistance.
- A compatible method to encapsulate the inhibitor should be investigated.
- The matrix, in which the inhibitor is added (capsulated or bare), should be resistant to alkaline conditions. It is suggested to select an alkaline resisting matrix.
Appendix A

A.1. LSV plots

A.1.1. GA steel

Figure A.1: GA steel LSV data for Ce(NO$_3$)$_3$
Figure A.2: GA steel LSV data for KI

Figure A.3: GA steel LSV data for MBT
Figure A.4: GA steel LSV data for Na₂MoO₄

Figure A.5: GA steel LSV data for Na₂SiO₃
Figure A.6: GA steel LSV data for Na$_2$WO$_4$

Figure A.7: GA steel LSV data for TiOSO$_4$
A.1.2. HSS

Figure A.8: HSS LSV data for Ce(NO₃)₃

Figure A.9: HSS LSV data for KI
Figure A.10: HSS LSV data for MBT

Figure A.11: HSS LSV data for Na$_2$MoO$_4$
Figure A.12: HSS LSV data for Na$_2$SiO$_3$.

Figure A.13: HSS LSV data for Na$_2$WO$_4$. 
A.2. Pourbaix diagrams

Figure A.14: HSS LSV data for TiOSO$_4$

Figure A.15: Pourbaix diagram for GA steel
Figure A.16: Pourbaix diagram for HSS
Figure B.1: Proof of ridging effect: Ridges make it difficult for light element (Z<11) to be detected. Black spots occur on the ridges and these spots change by rotating the sample 90 degrees. If the black spots are due to elements not occurring, the black spots would not have changed.
C.1. FTIR spectra

C.1.1. GA steel

Figure C.1: Normalized FTIR spectra with grazing element for GA steel samples immersed in 2 g/L sodium metasilicate and 0.05 M NaCl at different time intervals. Black dashed lines indicate silicate related peaks. Blue dashed lines indicate a base of the peak or a shoulder, as a tool to recognize peak shifts.
Figure C.2: (Continued) Normalized FTIR spectra with grazing element for GA steel samples immersed in 2 g/L sodium metasilicate and 0.05 M NaCl at different time intervals. Black dashed lines indicate silicate related peaks. Blue dashed lines indicate a base of the peak or a shoulder, as a tool to recognize peak shifts.
C.1.2. HSS

Figure C.3: Normalized FTIR spectra with grazing element for HSS samples immersed in 2 g/L sodium metasilicate and 0.05 M NaCl at different time intervals. Black dashed lines indicate silicate related peaks. Blue dashed lines indicate a base of the peak or a shoulder, as a tool to recognize peak shifts.
Figure C.4: (Continued) Normalized FTIR spectra with grazing element for HSS samples immersed in 2 g/L sodium metasilicate and 0.05 M NaCl at different time intervals. Black dashed lines indicate silicate related peaks. Blue dashed lines indicate a base of the peak or a shoulder, as a tool to recognize peak shifts.
C.2. FTIR surface measurement
Measurement of the surface area of the FTIR peaks were done by firstly correcting the the baseline of the raw data. Then the peak bases were allocated and a correction for the baseline was made (see figure C.5). The software automatically gave the values.

Figure C.5: Surface area measurement under the peak of an FTIR spectrum: The blue curve is the raw spectrum. The Red curve is raw data which has a corrected baseline. The small black triangles indicate the base of the peak. The black line indicates were the base is corrected for the peak.
Bibliography


