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STUDY OF CORROSION PROCESS OF SURFACE
HARDENED STRUCTURAL STEEL FOR APPLICATION IN
PETROLEUM INDUSTRY
Petroleum Technology Processes

Supervised by: Prof. Dr. Jochen Uebe

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ABSTRACT

In this Master thesis, the process of corrosion in S235 structural steel in sodium chloride solution, technological condensate of industry, and ammonium hydrogen sulphide was studied. The process of corrosion was investigated by the use of linear polarization resistance method. Surface hardening of the structural steel samples for reducing the corrosion rate such as carburizing and annealing were used during the research. The process of corrosion in the aggressive media like the sodium chloride solution, technological condensate and ammonium hydrogen sulphide was reduced by using two inhibitors, CHIMEC 1839 and Stearin dissolved in Toluene. The hardness of the structural steel samples (annealed, carburized and nitrided) were measured using the Vickers Hardness testing machine and an analysis of each kind of sample with respect to their rate of corrosion in all of the aforementioned aggressive media was studied, leading to a detailed conclusion at the end.

Contents include: 57 pages, 9 tables, 34 figures.

Key words: S235 steel, corrosion rate, corrosion inhibitors, annealing, carburizing, nitriding, hardness value, sodium chloride, ammonium hydrogen sulphide.

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INTRODUCTION

Corrosion is a universal problem. It is also of particular importance in the field of chemical plants and oil refineries. Usually, low alloyed carbon steel or structural steel is used owing to the structural steel being cheap, easily available and easy to manufacture. The structural steel is also inherently easier to work with when compared to high alloyed steels such as stainless steel. The environmental damage and economic loss to the refining industry is due to the fact that a large number of metal equipment and structures come into contact with a very aggressive environment. The presence of corrosive components in technological media is one of the main factors leading to emergency failures and premature equipment wear (Vagapov 2008).

It is therefore important to understand the principles of corrosion in order to efficiently select materials for the design, manufacture and use of metal structures for ensuring optimal, cost-effective, improved plant life and enhanced security of operations. (Chilingar 2008).

Objective of the work: To study the effect of aggressive media like sodium chloride solution, ammonium hydrogen sulphide and technological condensate on the corrosion process on S235 structural steel samples and to identify the best suitable ways by means of surface hardening and/or use of inhibitors to reduce the effect of corrosion in the samples.

Task of work:

1. To perform literature review on corrosion damage in oil refineries - types of corrosion, corrosion rate estimation methods and protection methods
2. To perform surface hardening of samples through carburizing and nitriding.
3. To determine the corrosion resistance of the treated S235 structural steel in sodium chloride solution, technological condensate and ammonium hydrogen sulphide with and without inhibitor.
4. To analyse the impact of aggressive media on S235 structural steel in order to identify the best suited method.

1. Literature review

1.1. Types of corrosion in refineries

According to Groysman (Groysman 2017), corrosion is a phenomena that occurs in any industry and anywhere: in water, atmosphere and soil at high temperatures, acid corrosion or corrosion of heat insulation. The author distinguishes the following types of corrosion: spot, slit, galvanic, intercrystalline, intergranular, selective leaching, cracks, microbial corrosion, erosion, cavitation and mechanical corrosion. Meanwhile, according to Sastri (Sastri 2011) corrosion can be of eight forms: general, point, intercrystalline, local, galvanic, crack, stress (SCC) and erosion-corrosion.

In terms of exposure and prevention of corrosive environments, any corrosive environment can be divided largely into two main categories: (a) liquid and solutions; (b) gas. When the corrosive environment consists of water with dissolved substances (salts and / or acids and / or bases), the liquid acts as an electrolyte, which is an electrochemical process. When the corrosive environment is dry gas, the environment is not conductive or in other words, the process is chemical corrosion of metals. A majority of cost involved when it comes to corrosion in the oil industry is due to electrolyte corrosion or wet corrosion. (Javaherdashti et al. 2013; Bardal 2003; Kaesche 2003; Groysman 2017).

Specific to petrochemical units and oil refineries, corrosion may be grouped into five groups (Groysman 2017):

- Corrosion at low temperature ($T < 100^{\circ}\text{C}$) in presence of electrolytes, which are usually water and aqueous electrolyte solutions consisting of dissolved gases like HCl and H₂S or dissolved salts like NaCl and Na₂SO₄. The corrosion rate is dependent on concentration of dissolved substances. In some concentrations, H₂S has a tendency for passivation (forming of passive protective film) on the surface of carbon steel. Both salts, i.e., NaCl and Na₂SO₄ at concentration of 3% accelerate the process of corrosion on the carbon steel at very high concentrations ($> 26\%$ by weight), while releasing dissolved oxygen; the carbon steel corrosion is zero.
- Corrosion at high temperature ($T > 200^{\circ}\text{C}$) under non-electrolytes (mostly H₂S and H₂ gas; naphthenic acid corrosion; hot ash corrosion; and oxidation of oxygen furnaces).
- Corrosion at moderate temperature ($100^{\circ}\text{C} < T < 200^{\circ}\text{C}$) which could be caused by electrolytes or non-electrolytes and it depends on the conditions and materials.

- Corrosion occurring in nature: atmospheric corrosion, soil and water bodies. In other words, areas where petroleum and oil refinery facilities and instalments come in contact with environment.

- Corrosion specific to certain phenomena: acidic corrosion, corrosion in heat insulation and steam condensate.

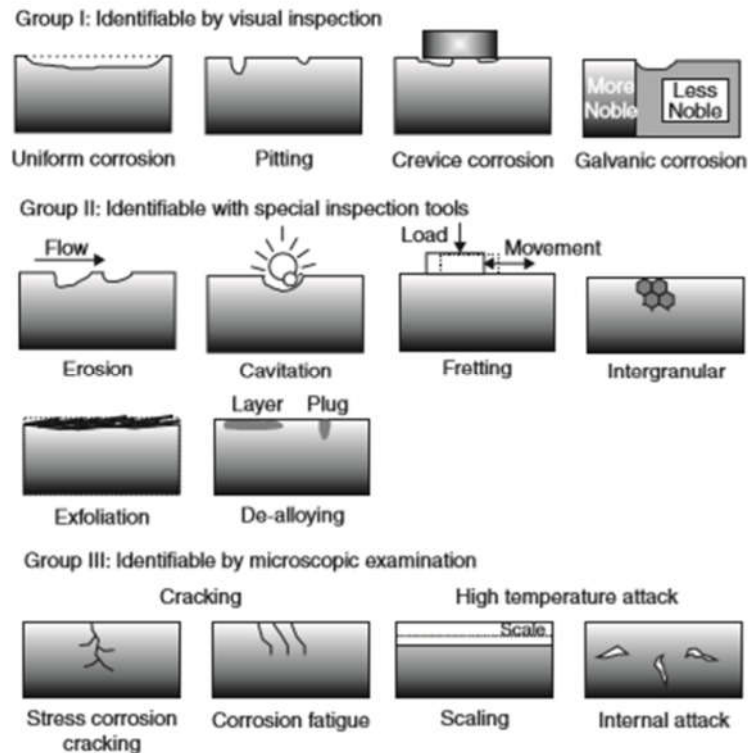


Fig. 1. Types of corrosion attack (Roberge et al., 2008)

Roberge et al. (2008) classified the forms of corrosion into three groups according to their mode of identification (graphically depicted in Fig. 1):

a) Corrosion damage that can be easily detected by visual inspection. These could be uniform corrosion, pitting, crevice corrosion and galvanic corrosion;

(b) Corrosion damage which may require further investigation. These are erosion, cavitation, fretting, exfoliation, intergranular corrosion and de-alloying;

(c) Corrosion which should be detected by one or the other type of microscope. These could be cracking due to stress corrosion, corrosive metal fatigue and due to high temperature, such as scaling and internal attack.

According to the nature of the metal damage, Kačerauskas (2006) classified corrosion into continuous and local corrosion. This corrosion often occurs in the oil industry pipelines but is usually the least damaging type of corrosion. (Chilingar, 2008; Nasirpouri et al., 2014). The anodic and cathodic regions are constantly changing, resulting in more or less uniform corrosion throughout the metal surface. Over time, the metal becomes thinner and weakens. This form of corrosion accounts for most of the destruction of metals. However, from a technical point of view, this is the only type of corrosion that is of least concern, mainly because the life of a metal can often be estimated with sufficient accuracy based on relatively simple corrosion tests. (Javaherdashti et al., 2013). Local corrosion covers only some areas of the metal surface (Kačerauskas, 2006).

Pitting is one of the forms of local corrosion, when grooves and grooves are formed on the metal surface as a result of environmental action. This type of corrosion often occurs in low pH saline solutions. With the formation of spot corrosion, the corrosion continues as a crack, but usually at higher speeds. (Chilingar, 2008). As Kaesche (2003) states, unlike continuous corrosion, which has a predictable rate, spot corrosion usually affects metal unexpectedly and at high speed. Mai et al. (2018) attributed this phenomenon of local corrosion to galvanic corrosion, where the actively decaying (corroding) region is the anode and the passive region is the cathode.

Crack corrosion - Local corrosion that occurs in areas of metal equipment, pipe and collar joints, rod legs and boxes, piping and drill pipes. Crack corrosion results from the difference in concentrations between the metal and the jointing material. Differences in electrochemical potential determine the intensity of crack corrosion. Cracked corrosion (contact corrosion) is most commonly caused by metal contact with a non-metallic material (Chilingar 2008).

Intergranular corrosion is the corrosion that occurs within the boundaries of metal grains, with no appreciable corrosion on the grains themselves. It is also described as local corrosion of metal or alloy within the grain contact range. The contact range of the grain is always anodic and the grain is cathodic. (Javaherdashti et al., 2013). Zhou et al (2016) suggest that the contact force between the grains is weakened during intergranular corrosion, which impairs the mechanical properties of the steel. Improper heat treatment of metal alloys or exposure to high temperatures can cause material wear or inhomogeneity within the grain boundaries of the metal structure, resulting in intergranular corrosion. Intergranular corrosion occurs at welding sites. The lesions occur in a narrow section on each side of the weld due to changes in compression-sensitive grain structure. Proper heat treatment or metal selection can prevent corrosion damage caused by welding (Chilingar, 2008). According to Javaherdashti et al (2013), this form of corrosion in stainless steel products can be avoided by annealing the equipment after welding and thus stabilizing the stainless steel or, more preferably, using low carbon ($\leq 0.03\%$) stainless steel grades.

Galvanic or two metal corrosion can occur when two different metals come into contact with the corrosion environment. This is usually local corrosion that occurs near the point of contact of the metals. (Chilingar, 2008). Galvanic corrosion often occurs when two different metals are exposed to an electrolytic solution. One of the metals is more active, has less potential, and therefore oxidizes and decays during galvanic corrosion. Meanwhile, less active, more expensive metal is protected. (Javaherdashti et al., 2013).

Selective leaching occurs when one component of the alloy is removed by a corrosion process. An example of this type of corrosion is selective zinc corrosion in brass. (Chilingar, 2008).

Damage caused by cavitation corrosion - appearance of sponge with deep pits on metal surface. Damage can be caused by mechanical action, whereby the pulsating pressure during evaporation causes evaporation with bubble formation and disintegration on the metal surface. Mechanical treatment of the metal surface causes damage that increases in a corrosive environment. (Chilingar, 2008).

The combination of erosion and corrosion causes enormous damage to the metal surface through two different processes - electrochemical corrosion and mechanical erosion. The total weight loss is usually greater than the sum of the weight loss caused by corrosion alone or by erosion alone (Zheng et al. 2015). The result of the process is a groove or hole in drill pipes, suction pipes, housings or pipelines. Completes the process of erosion and corrosion by metal destruction. The erosion process removes protective films on the metal surface, allowing the corrosive environment to affect the clean metal surface, which speeds up the corrosion process. (Chilingar, 2008).

Corrosive metal fatigue is a gradual decrease in metal durability due to cracks in the crystals under cyclic loading and adverse environmental conditions. In unfavorable environments, the process of corrosive metal fatigue is accelerated by electrochemical corrosion. Cracks (micro-cracks) appear on the surface of the metal and spread further (Kačerauskas, 2006; Roberge et al., 2008). The rate of corrosion is influenced by the oxygen content, pH, temperature and solution composition. The rate of corrosion is influenced by the oxygen content, pH, temperature and solution composition. Corrosion fatigue can be eliminated or reduced by heat treatment of structures using corrosion inhibitors as well as zinc, chromium, nickel, copper or nitrogen coatings. (Sastri, 2011).

Stress corrosion results from simultaneous tension and adverse environmental effects on metal surfaces. An example of stress corrosion is a tube, one part of which consists of a metal exposed to stress (anode) and the adjacent metal is not exposed to stress (a cathode). The degree of

stress corrosion in the pipeline varies with metallurgical properties, cold working, pipe weight, tool impact on the clamps, and the presence of H_2S gas. (Chilingar, 2008). The thermal stress caused by welding during production is the most common cause of stress corrosion. Proper selection of post-production stress relieving or annealing techniques is required based on the environment in which these materials will be used. In all cases, temperature and concentration are important factors. (Javaherdashti et al., 2013).

Hydrogen-induced damage (hydrogen fragility) is critical to the refining industry due to high temperature hydroprocesses (Speight, 2006). Corrosion reduces the strength, peak strength, and ductility of the product due to the accumulation of hydrogen in steel, which is known as hydrogen brittleness (Le et al., 2018; Eggum, 2013). The corrosion process is a combination of oxygen reduction and hydrogen release reactions. These reactions release atomic hydrogen. It then accumulates in steel voids or defects, forming molecular hydrogen. Molecular hydrogen increases the internal pressure and the likelihood of micro cracks, which deteriorates the mechanical properties of the metal. (Groysman, 2017; Javaherdashti et al., 2013; Le et al., 2018).

During the acidic corrosion process, H^+ ions occupy the released electrons of iron atoms to form atomic hydrogen. The two hydrogen atoms combine to form H_2 gas. However, the tendency to form H_2 gas is reduced if an iron sulfide film is present on the metal surface. Hydrogen atoms of very small size are dispersed into the steel matrix. If manganese sulfide is present in the steel, adsorption of atomic hydrogen takes place on the surface. Hydrogen atoms adsorbed on manganese sulfide are bound to H_2 gas. Because the size of the H_2 molecule is larger than atomic hydrogen, H_2 gas cannot escape. This causes a huge local pressure increase, which results in internal steel cracks (Javaherdashti et al., 2013).

Chlorides and sulphates increase the corrosivity of aqueous solutions by adsorbing on the metal surface to form highly soluble compounds. This increases the rate of steel corrosion and causes local corrosion phenomena, which are observed even during visual inspection (Nasirpour et al., 2014). The presence of metal chemical elements, such as calcium, magnesium, potassium, aluminum, manganese, silica and zinc, has confirmed the possibility of corrosive formation on the inner surface of carbon steel tubes in the process of electrical salt and water removal (Nasirpour et al., 2014).

In acidic media, the corrosion of carbon steels is accelerated due to the absence of a protective film on the metal surface, and the formation of iron oxides and hydroxides, or even iron carbonates, is not possible (Velazquez et al., 2018). KCl and $CaCl_2$, have a significant influence on the formation of local corrosion. The presence of chloride ions increases the fragmentation of the

passive layer, which increases the likelihood of a steady increase in cracks over time. In contrast, the presence of carbonate ions (CO_3^{2-}), an indicator of water hardness and alkalinity, increases the protective layers on the steel surface, which results in less corrosion (Velazquez et al., 2018).

1.2. Methodology used for monitoring and determining the process of corrosion

In the petroleum industry, it is of prime importance to detect defects caused by corrosion and to evaluate them. In order to ensure high levels of safety along with reliability, the pipelines, containers and their bottoms must be inspected periodically so that corrosion due to hazardous chemicals released into the environment can be prevented. The extent of corrosion can be minimized if the root cause of corrosion in the environment is determined. Control measures can be initiated to prevent serious damage with the help of rapid detection of active corrosion. It is also critically important to identify active corrosion before an untoward accident takes place. Under such circumstances, the rate of corrosion is to be measured (Sastri, 2011; Chilingar, 2008). However, according to Chilingar (Chilingar, 2008) if metal loss is insignificant, it is economically more favourable to allow the corrosion to persist than reducing or preventing it.

Monitoring systems can be used to routinely monitor the samples for corrosion, such as using portable data loggers, or comprehensive self-integrated devices that process and monitor systems by using remote access and control of data. (Sastri, 2011; Honarvar et al., 2013). Non-destructive test methods can be used for assessing the surface for internal metal damage without disrupting the operation of equipment (Dwivedi et al., 2018).

There are also integrated methods used for long-term monitoring of pipeline corrosion when a sensor device is inserted into a pipe where it is exposed to a corrosive environment. Various types of sensors are used for such technologies: specimens, electrical resistance, linear polarization, and galvanic sensing devices (Roberge et al., 2008).

Data collection for these methods is done offline and requires additional manpower to monitor the process (Roberge et al., 2008, Sastri, 2011). Most corrosion phenomena are electrochemical in nature and consist of reactions on a corroding metal surface, so electrochemical detection methods can be used to characterize corrosion mechanisms and predict corrosion rates. The power source polarizes the sample with corrosion potential and the resulting current is equal to the corrosion rate (Sastri, 2011).

Corrosion rate is usually expressed in one of the following ways:

- Weight loss per unit area per unit time;
- Penetration rate, that is, thickness of lost metal;
- Corrosion current density. The corrosion rate equals the removal of metal ions per unit area of metal per unit time.

This ion transport can be expressed as I_a , the electric current per unit area, i. e. the anode current density i_a equals the corrosion current density i_{corr} . ($i_{corr} = i_a = I_a / A_a$, where A_a is the anodic area), (Javaherdashti et al, 2013; Bardal, 2003).

1.2.1. Linear Polarization method (LPR)

Use of Linear Polarization Resistance (LPR) device for monitoring and measuring the electrochemical corrosion is an effective method to enable direct measurement of the real time rate of corrosion. Corrosion rate is calculated by monitoring relationship between the electrochemical potential and current generated between the electrically charged electrodes during this process. The current that is measured between these two samples will vary depending on the chemical composition of the samples or of the electrolyte. (Nazir 2018; Bardal 2003, Roberge et al. 2008).

This method of monitoring corrosion is widely used and measures the rate of corrosion with the use of a device which directly converts the data into imperial units of measure - mpy (Sastri 2011).

The LPR sensor may either be two or three electrode configurations with electrodes that are of pleated or protruding types.

The MS1500L is a hand-held, battery-powered, corrosion meter capable of measuring from all types of 2- electrode linear polarization resistance (LPR) corrosion probes (Fig. 1.).

The instrument measures the current required to polarize the electrodes of a probe to a known potential. From the polarization potential and the measured current, polarization resistance can be calculated. Then, using Faraday's law, the instantaneous corrosion rate can be calculated from polarization resistance.

The MS1500L incorporates a zero-resistance ammeter (ZRA) for measuring galvanic current between electrodes (Manual, MS1500L LPR Data Logger).



Fig. 2. MS1500L LPR device

Due to the electrochemical mechanism of metal / alloy electrode, when it is immersed in an electrolytic fluid that has oxidizing properties, it will corrode and this process involves two simultaneous and complementary reactions (Equations 1 and 2):



The metal moves from solid surface to liquid at the anodic sites while at cathodic sites, free electrons are absorbed by the corrosive fluid of material that oxidises (Zaki, 2006; Roberge et al., 2008).

The true value of the polarization current is the equilibrium value ΔI which occurs after the time interval T_c (Fig. 3.). The time delay ranges from 30 seconds and several hours, depending on the specific properties of the metal or the ambient system.

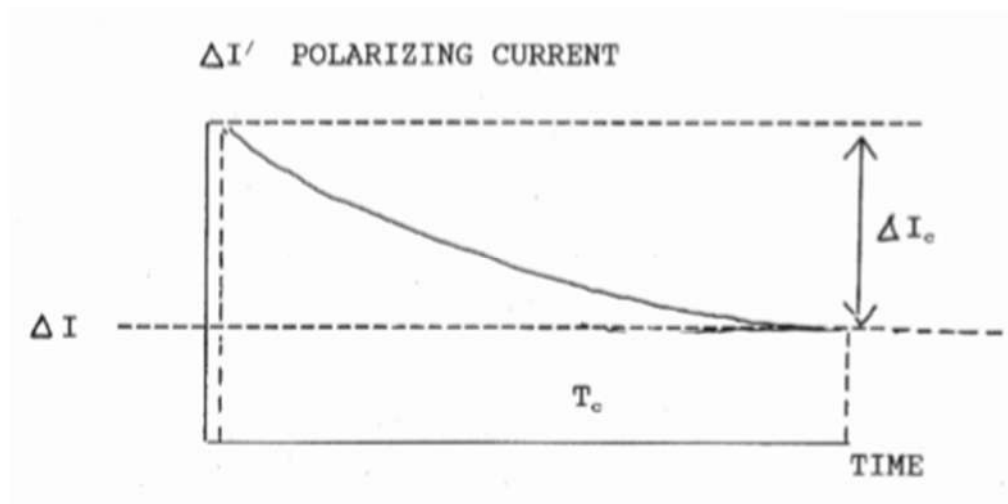


Fig. 3. Polarizing current vs. time in the MS1500L LPR device

linear polarization resistance (LPR) data for corrosion rate is valid only if the following conditions are met:

- one of the two reactions is cathodic and the other is anodic;
- the Tafel constants of anodic and cathodic parts are known and are constant;
- the surface is clean with no by-products of corrosion with no rough surface;
- there is continuous corrosion;
- there is low impedance in the solution;
- a stable value for corrosion potential is reached.

Such conditions are rarely achieved under actual industrial conditions (Sastri, 2011).

Some of the limitations of LPR technique are:

- The LPR method is used only in environment with a low impedance electrolyte and such a requirement prevents the use of this technique where the media has low conductivity like for example; refineries, oil and gas installations and chemical systems;
- the tube wall or sample must be submerged, which can lead to unsafe conditions and cause leaks;
- the corrosion coefficients as a result are approximate and this method is best suited only for conditions where there is a severe corrosion change (Sastri, 2011). It must be noted that a single method to monitor the process of corrosion in complex industrial activities will not suffice. It is therefore recommended that more (two or three) monitoring methods be utilised to justify any inaccuracy of one method to another technique of measurement (Sastri, 2011).

1.3. Corrosion protection methods in oil industry

The main methods of protecting metals from corrosion are the selection of corrosion-resistant materials for the manufacture of equipment and pipelines; to develop corrosion-resistant coatings, methods and treatment technologies for surfaces that are resistant to corrosion; and the development and use of corrosion inhibitors (Zagidullin et al. 2015).

Traditional "anti-corrosion" methods in the oil and gas industry Javaherdashti et al. (2013) divided into three categories:

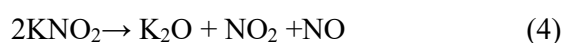
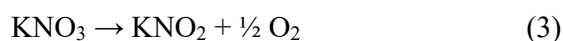
1. Modification of Special Purpose Equipment.
2. Reduction of corrosion intensity (inhibitors, cathodic protection).
3. Creation of interlayer between material and aggressive environment to avoid direct contact (various coatings).

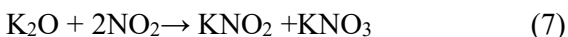
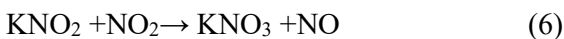
1.3.1. Thermochemical surface treatment

The properties of numerous metals and alloys rely upon the condition of its surface layer. Strengthening (hardening) this layer can further improve the mechanical properties of the material. Thermochemical treatment is a process of saturating the surface layers of metals with one or more elements that alter the chemical composition of the surface layer and get the desired surface properties and microstructure. Thermo-chemical treatment of metal increases its resistance to abrasion and environmental effects (corrosion, high-temperature oxidation, acids) (Czerwinski 2012).

Saturation and / or carbonization are traditional thermochemical surface treatment methods used to harden steel surfaces (Hamdy 2011). Conventional liquid nitriding (600 C) can improve the surface hardness and tribological properties of stainless steels. However, corrosion resistance is significantly reduced due to the precipitation of chromium nitride (Zhang et al., 2018).

Stainless Steel is increasingly gaining consideration because of its appropriate mechanical and corrosive properties. Various types of Stainless Steel are used in sectors such as railways, energy industry, shipbuilding, chemical equipment, oil and nuclear industries. Nitrogen behaves as an effective austenite stabilizer which greatly improves the strength of the steel and fracture toughness, along with improving resistance to spot corrosion. Nitrogen obtained from thermal decomposition reactions (Zhang et al., 2016; Vilys et al. 2007; Shen et al. 2006) is required for saturation:

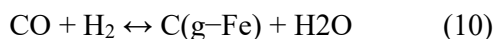
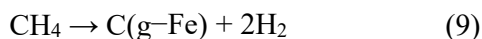
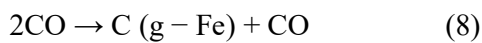




Nitrogen atoms penetrate the metal surface during saturation, thereby increases the hardness and corrosion resistance of the metal, in turn leading to an increase in life of the part. The increased hardness is by the formation of iron nitrides. (Prakash et al. 2018; Shen et al. 2006).

According to Saleh (2013), among various surface treatments, carburization is more attractive because of its many advantages. Carburization can increase the life, reliability and safety of parts.

Carburization is a thermochemical surface hardening process that saturates the surface of a material by diffusing carbon atoms to surfaces at high temperatures. Carburization can be performed in solid, liquid or gaseous media. The saturation medium is called a carburizer (Saleh et al., 2013; Vilys et al., 2007). The treatment is carried out at 900-950 °C to achieve sufficient carbon penetration depth. Such carbon is formed by dissociation of carbon monoxide or methane gas (Czerwinski, 2012):



The process of carburization depends on the composition of the carburizing environment, the carburization regime (temperature and duration), the composition and structure of the metal to be saturated, and the subsequent heat treatment. Carburized products are cooled, then quenched by heating to a temperature of 760-780 °C and then released at low temperatures (Czerwinski, 2012; Vilys et al., 2007).

Carburization (carburization and saturation) is carried out at high temperature by simultaneously saturating the steel surface with carbon and nitrogen. The distribution of carbon and nitrogen in the saturated layer depends on the process temperature. At lower temperatures, more nitrogen is saturated, and at higher temperatures, carbon saturation is predominant (Czerwinski, 2012; Vilys et al., 2007; Wang et al., 2011).

1.3.2. Use of inhibitors

One of the most known methods to reliably yet cost effectively protect metals from corrosion in oil and gas pipelines is the use of organic inhibitors. (Askari, 2018; Solmaz et al. 2007).

Inhibitors are bipolaric organic compounds (liquids) with various heteroatoms: N, P, S, O and high molecular weight (amides, amines, heteroalkyl four-valor ammonium and phosphorus compounds, high molecular weight acetylated alcohols , aldehydes, etc.). The film-forming inhibitors have a high surface activity and are chemically absorbed on all metallic surfaces (Esmaeilnia et al. 2014; Heydari, 2012).

Inhibitors with metal ions form poorly soluble compounds. These compounds form a protective film on the metal surface and protect against H₂S, NH₃, O₂, CO₂, organic and mineral acids and salts (Salim, 2018). Corrosion slows down due to a decrease in the active surface of the metal and also in the activation energy of electrohydraulic reactions, limiting the complex corrosion process (Fawzy et al., 2018). As mentioned by Mehdaoui et al. (Mehdaoui et al., 2016), the inhibitory properties remain good even in the emulsion with water.

The corrosion inhibition efficiency can be evaluated from the corrosion current densities values using the relationship

$$\eta_{pp} = \left[(i_{\text{corr}}^0 - i_{\text{corr}}) / i_{\text{corr}}^0 \right] \times 100 \quad (11)$$

where i_{corr}^0 and i_{corr} are the corrosion current densities values without and with inhibitor, respectively (Ouakki M. et al., 2018).

Imidazoline being a product of Diethylenetriamine (DETA) and fatty acid reactions, is obtained in two phases. The fatty acids are derived by the Amidoamine components when they are exposed to high temperatures of 160 ° C for 1-2 hours. Imidazoline is derived when amidoamines are heated at 240 ° C, 2-4 h (Askari, 2018). Imidazoline derivatives are the most commonly used (Zhang et. Al., 2015) and effective (Wahyuningrum et. Al., 2008) in the petroleum industry. The mechanism of corrosion inhibition on the surface of metal with the derivative compounds of imidazoline consists of two steps: transfer of inhibitor molecules over the metal surface, followed by the interaction of functional groups of the inhibitor with the Metal surface, shown as (Wahyuningrum et. Al., 2008):

-The "head" part of Imidazoline is the imidazoline ring scaffold which can be attached to the metal surface via the electron pair of nitrogen from the imidazoline ring.

-The "tail" part of Imidazoline, being the long hydrophobic alkyl chain that is present as a substituent of the imidazoline ring.

The inhibitor CHIMEC 1839-is a film-forming corrosion inhibitor. With electrostatic adhesion, complex molecules form a protective layer on any metal surface of the device.

Such materials can separate the metal from the water phase and therefore prevents the emergence of corrosion. The resulting film slows down the corrosion process because:

- Increased anodic or cathodic polarization (or both)
- Reduces ion diffusion to the surface of the metal;
- An increase in electrical resistance between the metal and the electrolyte;
- Increase in hydrogen overvoltage (Roberge et al., 2008).

CHIMEC 1839 protects against corrosion (even in dry areas), which occurs due to the effects of HCl, H₂S, O₂, organic acids, CO₂, HCN.

The CHIMEC 1839 is used for various types of corrosion and provides extremely low corrosion rate (less than 0.1 mm/year) and a low level of the required reagent CHIMEC 1839. (Шильников и др., 2016).

According to Ayello F et al (Ayello F et al. 2001) myristic acid can be used as corrosion inhibitor. Since we did not have myristic acid we substituted it with stearic acid. As stearic acid is dissolvable in warm toluene we used this solution as an alternative corrosion inhibitor to Chimec 1839.

1.3.3. Corrosion of surface hardened steel in aggressive electrolytes

Both nitriding and carburizing lead to increased corrosion resistance in stainless steel (more positive corrosion potential and decreased resolution currents) (Mani, et. al., 2017; Cajner, et. al., 2015; Yeh et. al., 2011). No sufficiently publications have been found to suggest this for unalloyed steels. According to (Scalera, et. al., 1993), low-alloyed and carbon steels treated by a liquid nitriding process and subsequent oxidizing deterrent baths show more even corrosion while simultaneously reducing pitting compared to untreated Steels. Ions nitrated, low-alloyed and carbon steels recorded worse corrosion resistance than the untreated steels. Potentiodynamic polarization tests of liquid nitride-treated 1020 steels in aerated 5 weight-% NaCl solution at pH 4 showed an anodic shift in corrosion potential of several hundred millivolts. This shift brought the corrosion potential into the passive range, where the reduction in current density indicates better corrosion

resistance of coupons treated with the liquid nitriding process compared to their untreated counterparts.

A specific kind of crude oil is shown in (Efird et. al., 1989) to have a significant impact on the corrosion of steel in crude oil/solar production. The addition of crude oil to brine lowers the measured rate of corrosion for steel exposed to the mixture, but different crude oils can have significantly different effects on steel corrosion at the same brine composition. The primary effect of crude oil on steel corrosion in crude oil/brine mixtures appears to be the protective effect of corrosion product layer formed on the steel. The algebraic product from the organic nitrogen concentration in weight percent and the acid count has an inverse relationship to the rate of corrosion in steel.

According to (Ayello et. al., 2011) it has been confirmed that some, not all, surface oil compounds inhibit corrosion. They are collected by flowing across the surface while changing the flow of the oil-water mixture. The effect of various inhibitors was also confirmed to depend heavily on their chemical nature. However, the contained surface-active compounds must not be present as free acids (Meriem-Benziane et. al., 2017), as they are very corrosive.

2. Research methodology

2.1. Scheme of experiment

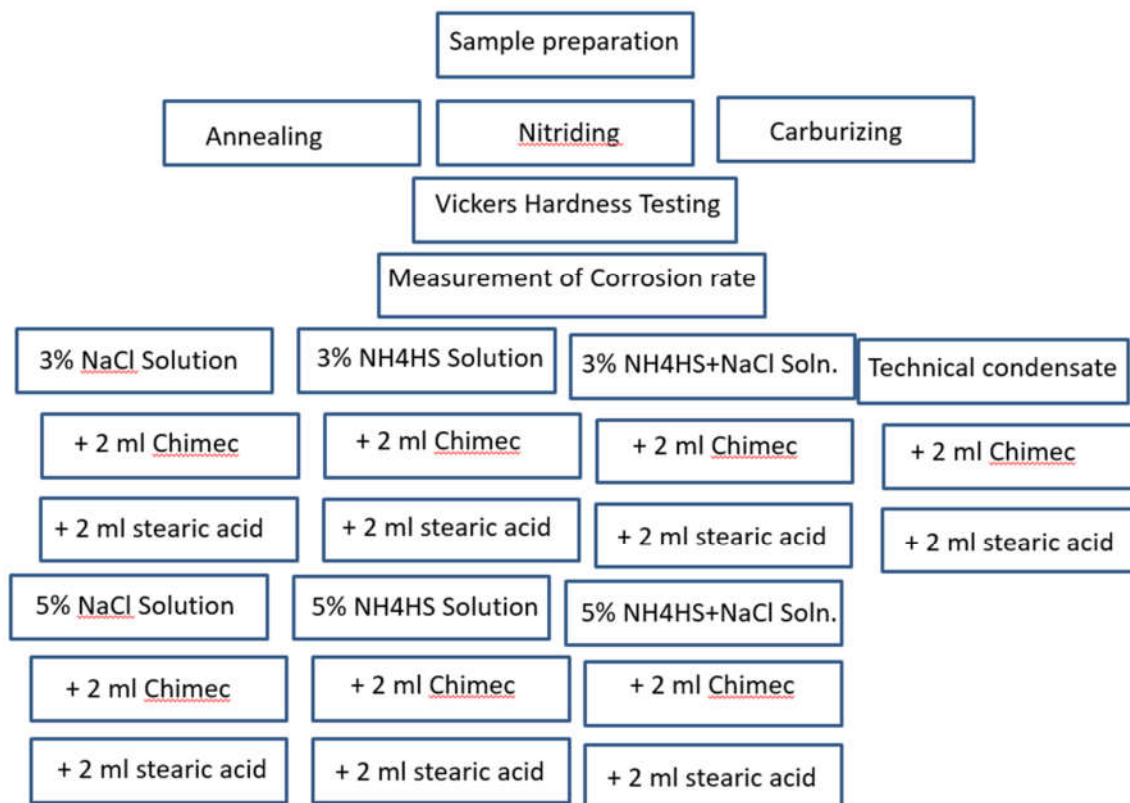


Fig. 4. Experimental Scheme

Scheme of experiment:

- At first, the metal samples were sanded down with grit papers of varying grain sizes.
- Some of the metal samples were annealed, others were carburized and the remaining samples were nitrided.
- The hardness value of each kind of metal samples were measured and duly noted before the start of each experiment.
- The corrosion rate of the different metal samples were measured under different electrolytes with the help of a LPR data recorder. The rate of corrosion in annealed, carburized and nitrided steel samples under varying concentrations of aggressive media with and without inhibitors; and also under the technological condensate obtained from ORLEN Lietuva were measured over a time span of 3 hours in the first day of measurement, followed by a set of measurement after 12 hours and the last set of measurement scheduled after 24 hours from the 12th hour reading. This routine was maintained in order to have a consistency in the measurement conditions, ensuring better repeatability of results.

- To assess the rate of corrosion in varying concentrations of electrolytes, the rate of corrosion was first measured in presence of 3% concentration NaCl, followed by that in 5% NaCl solution. This was done to see the tendency of corrosion over time when the samples were immersed in an aggressive corrosive media.
- The surface corrosion is removed by using the "Justy" wheeled polishing machine before harness testing was done in order to make the surface visible for the indentation of the probe of the Vickers hardness machine under the microscope.
- The hardness level of each kind of metal samples were consistently recorder using the Vickers hardness machine to verify the working of the process of corrosion.
- Next, the NaCl electrolytes (both 3% and 5% concentrations) were mixed with 2 ml of Chimec 1839 inhibitor. The corrosion rate for the different treated metal samples were measured.
- After the customary hardness value testing following the corrosion rate measurement was carried out, the inhibitor was changed to 2ml of 20/80 Stearic acid/Toluene inhibitor and consequent corrosion rate measurements were done for all the steel samples under 3% and 5% concentration levels of NaCl.
- The above steps were repeated for the laboratory prepared NH₄Hs electrolyte in both 3% and 5% concentrations.
- Similar tests were also done under the immersion of the steel samples in technological condensate.
- The results were then compiled and further analysed to reach the conclusions that will be found in this thesis.

2.1.1. Hardening of metal samples (carburizing and nitriding)

Metal samples of S235 structural steel

Table 1. Composition of S235 structural steel (Glinskiene, 2018)

C%	Si%	Mn%	S%	Cr%	Co%	Cu%	Ni%	Mo%	Fe%
0.24	0.26	0.52	0.06	0.13	0.01	0.69	0.32	0.03	97.64

Sanding down the metal samples with sand paper (P120, P180, P240, P800, P1000, P1200). It is then followed by use of wheeled polishing machine (Justy, India) for a perfect surface finish before subjecting the metal samples to surface treatment.



Fig. 5. Metal samples before sanding down



Fig. 6. Metal samples before sanding down

Annealing

In order to make the metal stable and without internal tension, all specimens were heated in a furnace (Typ L5/11/B180, Nabertherm) at 850 °C for 2 hours. The samples were left slowly to cool and subsequently tempered-re-heated at a temperature of 150 °C in a thermal furnace for 2 hours.

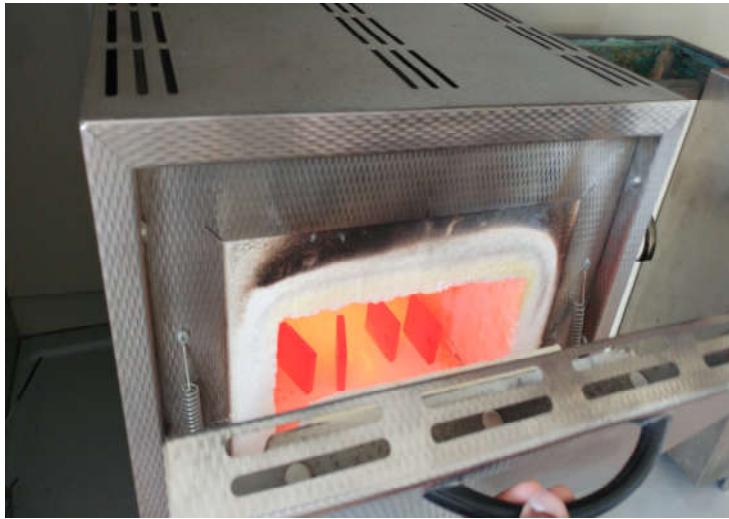


Fig. 7. Annealing of steel samples

Carburizing



Fig. 8. Closed container (seen here with the lid open) to prevent oxidation of charcoal

Carburizing (Fig. 8.) of samples were carried out by adding the samples to a steel bath with a closed top which was fully filled with lumps of charcoal.



Fig. 9. Heated in a thermal furnace, at 900 °c for 2 hours.

Quenching

The carburized samples were quenched by plunging them quickly into a cold water bath.



Fig. 10. Quenching of carburized samples

Nitriding

2Kg of Potassium Nitrate salt (KNO_3 , purity 99%, UAB Emolus (Kaunas, Lithuania)) was poured into a tub big enough to heat treat at least 3 samples at once.

The temperature being set to 640°C and the time of 8 hours.

Subsequently, the samples were brought down to room temperature in the nitration bath and then released.



Fig. 11. Nitriding of samples in Potassium Nitrate Salt



Fig. 12. The nitrided metal samples post release from the bath

2.1.2. Polishing metal samples with Polishing wheel

The polishing wheel was used for removing adhering oxide layers on the metal samples. The samples were polished every time the electrolyte was changed. The disc was covered by a felt cloth.



Fig. 13. Wheeled polishing machine; (Justy (india))

2.2. Methodology of conducting experiment

Preparation of sodium chloride electrolytes

30 or 50 g sodium chloride (NaCl , 99.9%, LACHEMA (Czech Rep.)) was dissolved in 1 litre of water for 3 or 5% solution.

Preparation of ammonium hydrosulphide

As in Fig 14 presented, a line of glass flasks of 300 ml and 500 ml at the end was connected as shown in Fig 15.

Two charges of 250 ml of a 3 % ammonium hydrosulphide solution was produced. Therefore, 51.68 g sodium sulphide ($\text{Na}_2\text{S} \cdot x\text{H}_2\text{O}$, $\geq 60\%$, Sigma-Aldrich) and 77 ml 35% hydrochloric acid (HCl , LACHEMA (Czech Rep.)) was filled in the first flask. The second and the fourth flask rested empty as a safety flask. The third flask contains 46.01 ml 16.3% ammonia solution (NH_3 , LACHEMA (Czech Rep.)) and 203.99 ml water yielding a 3% ammonia solution. The last flask contains an iron(III) chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\geq 99\%$, Riedel-de-Haën) solution for absorbing rest gas.

Sometime after the start of the reaction, the gas flow was supported by a pump for 2 minutes.



Fig. 14. Basic setup (NaCl in this case) for measuring the corrosion rate of the metal samples

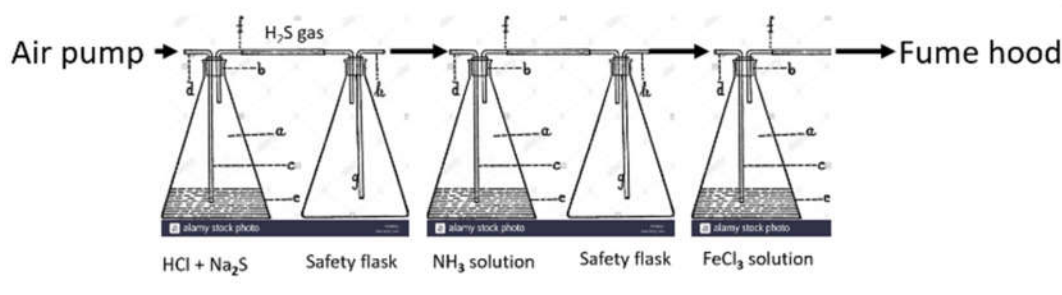


Fig. 15. Scheme of Ammonium Hydrosulphide preparation process

Preparation of mixture of ammonium hydrosulphide and sodium chloride solution

Into a fresh prepared ammonium hydrosulphide solution the required amount of sodium chloride was added.

Preparation of Chimec added electrolyte

Into the fresh prepared electrolyte 2 ml Chimec 1839 (CHIMEC S.p.A., Italy) (Glinskiene, 2018) per litre electrolyte was added.

Preparation of stearic acid added electrolyte

Firstly, a solution of 20 g stearic acid ($C_{17}H_{35}COOH$) in 80 g toluene (C_7H_8 , $\geq 99.7\%$, Sigma-Aldrich) was dissolved by heating and stirring.

Into the fresh prepared electrolyte 2 ml of the stearic acid/toluene solution per litre electrolyte was added.

Composition of technological condensate of ORLEN Lietuva: (Glinskiene, 2018).

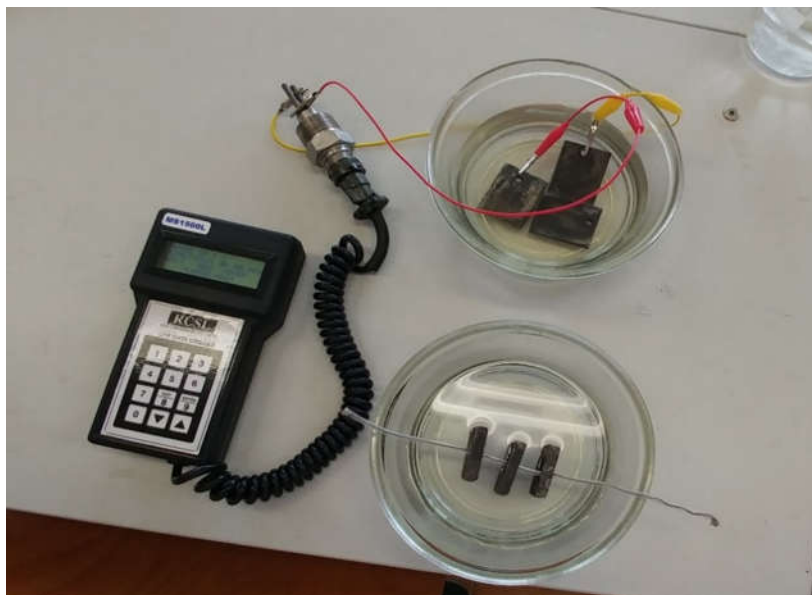


Fig. 16. Setup for measurement of corrosion at atmospheric conditions

Measurement of corrosion in sodium chloride solution and technological condensate was done at atmospheric conditions.

Measurement of corrosion in ammonium hydrogen sulphide and mixtures of ammonium hydrogen sulphide and sodium chloride were done in closed containers to avoid evaporation of ammonia and hydrogen sulphide. The containers were closed because of the instable nature of ammonium hydrogen sulphide. The conversion of the salt is according to (Holleman A. F., Wiberg N., 1995) the salt illustrated below displaying an ease of achieving equilibrium:



Where ammonia and hydrogen sulphide volatilise continuously and therefore the reason for their very strong and unpleasant smell (also called “stink bomb”). This would lower with concentration over time.

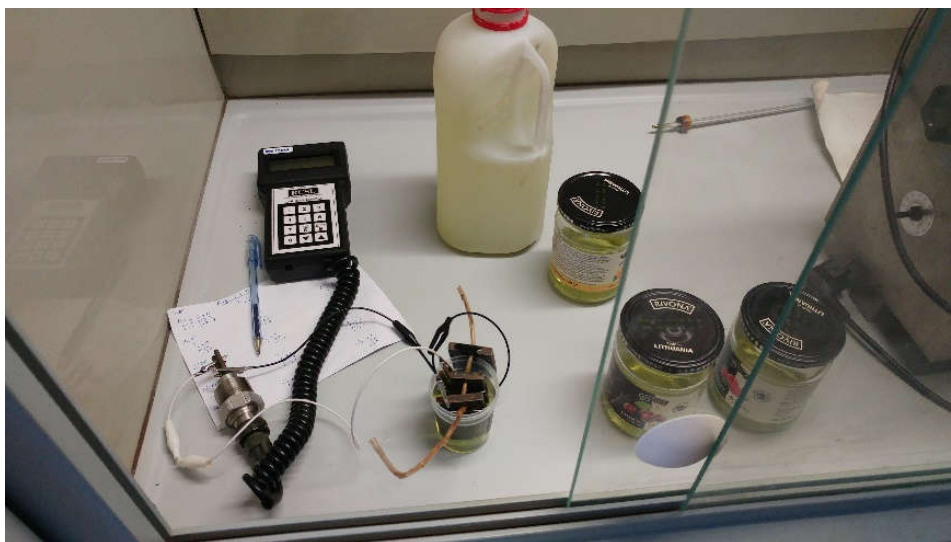


Fig. 17. Measurement in the fume hood

Corrosion rate determined by MS1500L (Metal samples company, USA).

The 3% solution is to be compared with literature, while the 5% to be compare with technological condensate

Measurement of hardness by Vickers hardness testing machine (Volpert Wilson 430 SVA) according to ISO 6507-1



Fig. 18. Vickers hardness testing machine (Wolpert Wilson 430 SVA)

The Wolpert Wilson 430 SVA is Vickers Hardness tester that has an analogue micrometre.

A 10 Kgf load was set for the diamond indenter on the machine to make the indent on the metal surface.

3. Results and discussion

3.1. Results of the investigation of corrosion resistance of S235 structural steel in aggressive media

3.1.1. Comparison between different concentration of pure electrolytes and added with the corrosion inhibitors

Solution of sodium chloride as electrolyte

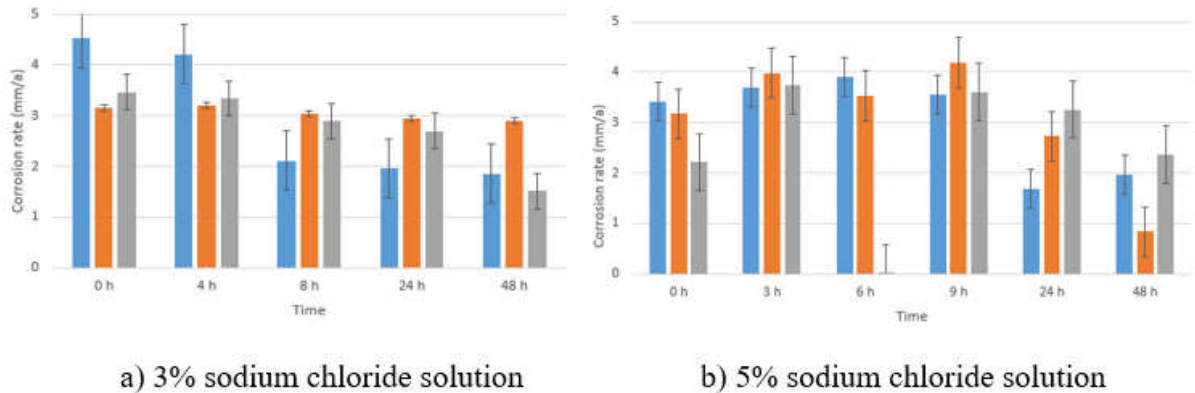


Fig. 19. Averaged corrosion rates of ●=annealed, ●=carburized, ●=nitrided steel samples over time

The surface hardening of samples inhibit the process of corrosion. It is a kind of passivation layer. Therefore it is also possible to calculate the inhibitor efficiency for surface hardened steel samples.

Inhibitor efficiency of surface hardened steel samples in relation to the non-surface hardened steel (annealed steel) calculated according formula 11 on page 15 (applicable for the rest of the cases as well):

Inhibitor efficiency of carburized steel in 3% solution of sodium chloride at initial state ($t = 0$ h) is 30.61 % in relation to annealed steel, of nitrided steel is 23.61%.

Inhibitor efficiency of carburized steel in 5% solution of sodium chloride at initial state ($t = 0$ h) is 7.14 % in relation to annealed steel, of nitrided steel is 30.21%.

In the 5% salt solution a trend of decreasing corrosion is noted, whereby the annealed steel decreases the most, followed by the nitrided and finally the carburized steel. This trend can hardly be seen in the 3% salt solution.

In the presence of 5% NaCl, the readings varied drastically but the readings showed expected results in presence of 3% NaCl which shows passivation as the corrosion rate dropped in time.

Solution of ammonium hydrosulphide

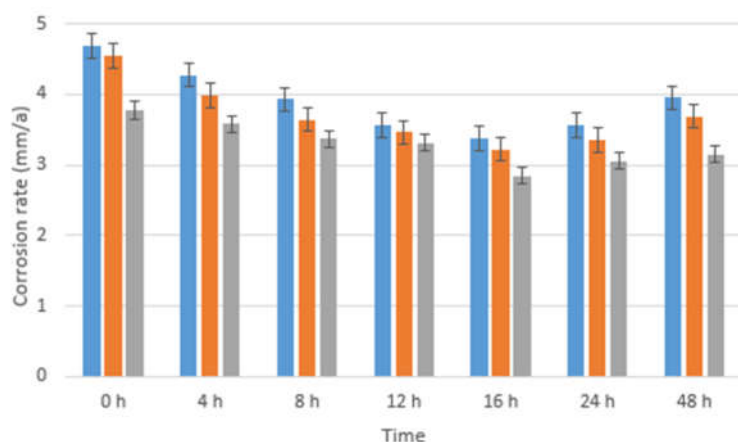


Fig.20. Averaged corrosion rates of ●=annealed, ●=carburized, ●=nitrided steel samples in 3% solution of ammonium hydrosulphide over time

Inhibitor efficiency of carburized steel in 3% solution of ammonium hydrosulphide at initial state ($t = 0$ h) is 3.26 % in relation to annealed steel, of nitrided steel is 19.69%.

Corrosion in ammonium hydrosulphide is more pronounced than in the analog Brine solution. Here you can see a decreasing trend that is the same for all three steel types.

A measurement in the 5% ammonium hydrosulphide solution was not possible for technical reasons. Due to the high salt concentration, the conductivity was probably so high that a constant current was always formed between the electrodes within the sampling rate.

The measuring device measures the decrease between the first and last current measured values of a specified measuring time and converts this into the corrosion rate. This explanation is particularly valid for all subsequent measurements where no measured value can be shown.

Mixture of solution of sodium chloride and solution of ammonium hydrosulphide

In both cases of the mixture of sodium chloride solution and ammonium hydrosulphide solution in 3% as well a 5% concentration levels, measurement using the LPR device was not possible for technical reasons, like the previously speculated high sampling rate due to high concentration of the solution.

Out of the two solutions, we can make an educated speculation from previous readings, that the main reason for the non-showing of reading due to high concentration could be due to the presence of ammonium hydrosulphide, as in the case of sodium chloride solution, we were able to measure the corrosion rate using the LPR device for both concentrations (3% as well a 5%) whereas with ammonium hydrosulphide, the measurement was only possible at 3% concentration.

Perhaps, the added concentration of sodium chloride along with that of ammonium hydrosulphide gave affected the measurement of the corrosion rate of the mixture of the two electrolytic solutions.

Solution of sodium chloride + 0.002 % Chimec 1839

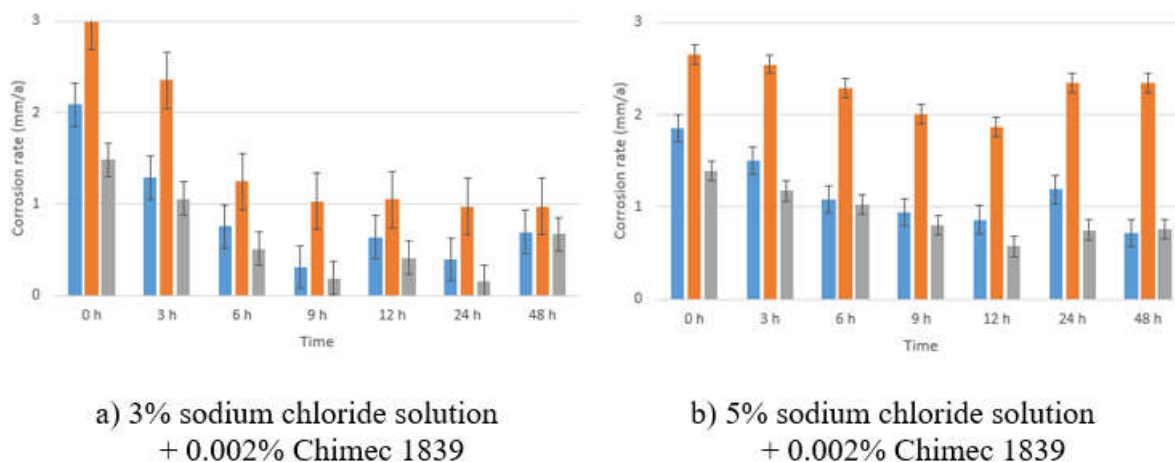


Fig.21. Averaged corrosion rates of ●=annealed, ●=carburized, ●=nitrided steel samples over time

The addition of Chimec leads to a reduction in the corrosion rate in both NaCl solutions, whereby nitrided steel is protected the most and to a lesser extent annealed steel from corrosion. Carburized steel is comparatively little protected.

The inhibitor efficiency by surface hardening of carburized steel in 3% solution of sodium chloride at initial state ($t = 0$ h) with 0.002 % Chimec 1839 is -43.25 % in relation to annealed steel, of nitrided steel is 28.79%. In analogue way the inhibitor efficiency of carburized steel in 5% solution of sodium chloride at initial state ($t = 0$ h) with 0.002 % Chimec 1839 is -42.97 % in relation to annealed steel, of nitrided steel is 25.02%.

This means that surface hardening already acts as a protection against corrosion. In particular, a nitrided surface together with Chimec provides better protection than an untreated surface. Carbon hardening has a protective effect in comparison with an undoped salt solution, but it obviously reduces the effectiveness of Chimec in comparison with an untreated sample.

The effect of the Chimec itself (itself) within a steel grade, i.e. only annealed or only nitrided or only carburized steel, is highest for annealed steel in the 3 and 5% salt solution. The effect of Chimec in carburized steels is comparatively low (Table 2.). The idea of the mechanism of action of the Chimec or the alkyl imidazole contained in it means that the imidazole adheres to the surface and creates a hydrophobicity with the alkyl tail. This mechanism probably hardly works on

carburized steels. One could probably measure by determining the binding energy between imidazole and nitrided, carburized or untreated steel.

Table 2. Efficiency of the corrosion inhibitor Chimec1839 in relation to the electrolyte without Chimec1839. The comparison can only be calculated for the same treated steel samples

Steel	3% solution of sodium chloride	5% solution of sodium chloride
Annealed	54.07%	45.75%
Carburized	5.17%	16.47%
Nitrided	57.18%	37.23%

Solution of 3% ammonium hydrosulphide + 0.002 % Chimec 1839

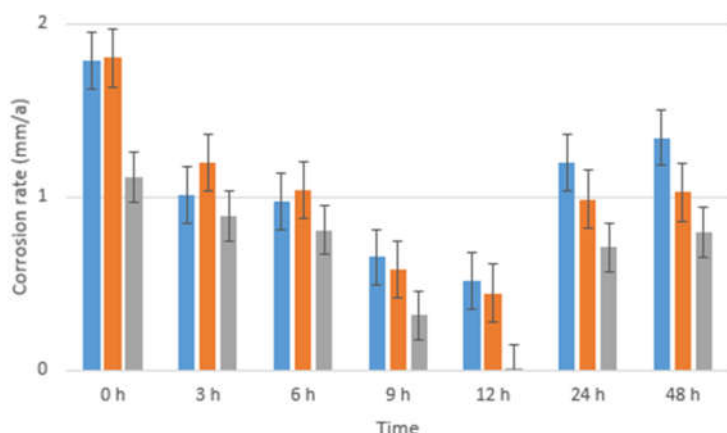


Fig.22. Averaged corrosion rates of ●=annealed, ●=carburized, ●=nitrided steel samples in 3 % solution of ammonium hydrosulphide with 0.002 % Chimec 1839 over time

Inhibitor efficiency of carburized steel in 3% solution of ammonium hydrosulphide at initial state ($t = 0$ h) with 0.002 % Chimec 1839 is -0.87 % in relation to annealed steel, of nitrided steel is 37.63%.

As expected, the corrosion rate in all cases reduced significantly with nitrided samples showing the most reduction in rate of corrosion, followed by that of carburized samples, with the least reduction or effect of inhibitor on annealed steel in presence of ammonium hydrosulphide.

Special mention has to be made for a briefly drastic reduction of rate during ($t=3$ h) and ($t=6$ h) of annealed samples. The only explanation for this could be an unstable passivation layer that might have formed due to a higher corrosion rate compared to the surface treated steels. The effect of passivation subsided with subsequent readings, meaning the layer was not very stable.

As stated in previous readings, in case of 5% solution, the conductivity was probably so high that a constant current was always formed between the electrodes within the sampling rate, thereby not giving a desired reading.

Table 3. Efficiency of the corrosion inhibitor Chimec1839.

Steel	Efficiency
Annealed	62.00%
Carburized	60.38%
Nitrided	70.49%

Mixture of solution of sodium chloride and solution of ammonium hydrosulphide + 0.002 % Chimec 1839

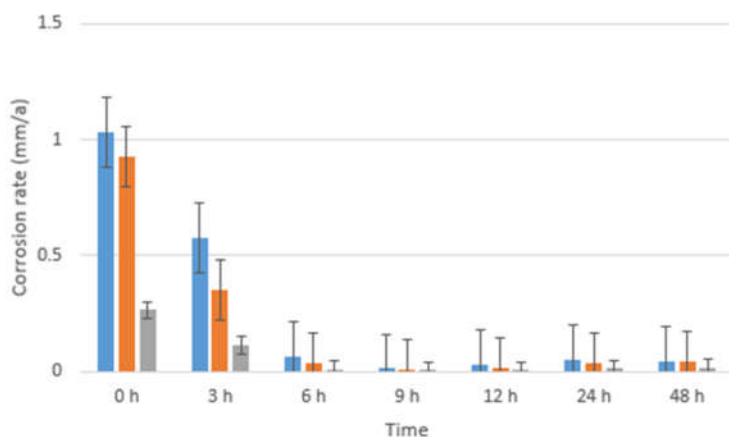


Fig.23. Averaged corrosion rates of ●=annealed, ●=carburized, ●=nitrided steel samples in a mixture of 3 % solution of sodium chloride and 3 % solution of ammonium hydrosulphide with 0.002 % Chimec 1839 over time

Inhibitor efficiency of carburized steel in 3% solution of sodium chloride and 3% solution of ammonium hydrosulphide at initial state ($t = 0$ h) with 0.002 % Chimec 1839 is 10.34 % in relation to annealed steel, of nitrided steel is 74.31%.

For 3% solution in presence of “Chimec 1839” inhibitor, a drastic reduction in corrosion rate in all cases of steel samples were observed, with nitrided steel samples showing the biggest change (decreased the most) compared to carburized as well as annealed samples, although it must be noted that the trend between the carburized and annealed steel samples at ($t=48$ h) largely remained the same, which goes on to show that “Chimec 1839” works the best with nitrided samples and the effectiveness of the inhibitor on the annealed and carburized samples although very much

noticeable in general, there was hardly any advantage of the carburized sample over the annealed sample in this case.

No measurement possible for 5% concentration of the mixture of solutions of sodium chloride and ammonium hydrosulphide even with the “Chimec 1839” inhibitor.

Solution of sodium chloride + 0.002 % Stearic acid/Toluene solution

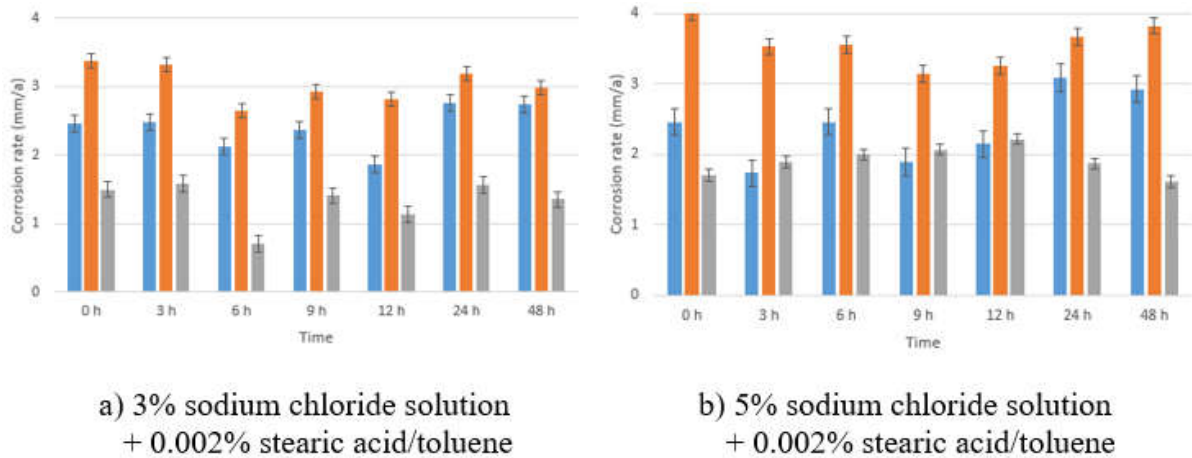


Fig.24. Averaged corrosion rates of ●=annealed, ●=carburized, ●=nitrided steel samples over time

Inhibitor efficiency of carburized steel in 3% solution of sodium chloride at initial state ($t = 0$ h) with 0.002 % Stearic acid/Toluene solution is -37.14 % in relation to annealed steel, of nitrided steel is 39.18%.

The nitrided steel samples like in most cases showed the biggest change in rate of corrosion, but surprisingly in both cases of 3% as well as 5% concentration of sodium chloride solution in presence of the inhibitor “stearic acid/toluene” worked better with annealed samples than with the carburized samples.

Inhibitor efficiency of carburized steel in 5% solution of sodium chloride at initial state ($t = 0$ h) with 0.002 % Stearic acid/Toluene solution is -63.47 % in relation to annealed steel, of nitrided steel is 30.63%.

The trend of corrosion for both 3% as well as 5% concentration across the samples were observed to be largely similar.

Table 4. Efficiency of the corrosion inhibitor Stearic acid/Toluene solution in relation to the electrolyte without Stearic acid/Toluene solution. The comparison can only be calculated for the same treated steel samples

Steel	Efficiency in 3% solution of sodium chloride	Efficiency in 5% solution of sodium chloride
Annealed	45.80%	28.08%
Carburized	-7.11%	-26.62%
Nitrided	56.85%	23.01%

(Note: The negative sign of efficiency denotes the inefficiency and not actual mathematical meaning.)

Solution of ammonium hydrosulphide + 0.002 % Stearic acid/Toluene solution

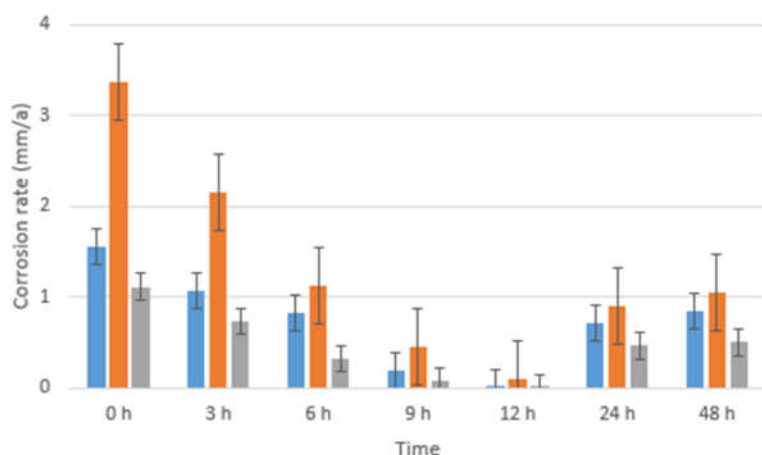


Fig.25. Averaged corrosion rates of ●=annealed, ●=carburized, ●=nitrided steel samples 3% solution of ammonium hydrosulphide with 0.002% stearic acid/toluene solution over time

Inhibitor efficiency of carburized steel in technological condensate at initial state ($t = 0$ h) with 0.002 % Stearic acid/Toluene solution is -115 % in relation to annealed steel, of nitrided steel is 28.43%.

The inhibitor “stearic acid/toluene” worked quite well in inhibiting the corrosion rate in the case of the aggressive media being 3% solution of ammonium hydrosulphide with the most inhibitive effect showed on the nitrided steel samples, followed by annealed samples. Although the inhibitor as it should, worked across all the types of samples, the effect was least noticeable on the carburized steel samples when in comparison with nitrided or even annealed steel samples.

No measurements were possible in 5% solution of ammonium hydrosulphide even in presence of the inhibitor “stearic acid/toluene”.

Table 5. Efficiency of the corrosion inhibitor Stearic acid/Toluene solution in relation to the electrolyte without Stearic acid/Toluene solution. The comparison can only be calculated for the same treated steel samples

Steel	Efficiency in 3% solution of ammonium hydrosulphide
Annealed	66.88%
Carburized	26.07%
Nitrided	70.48%

Mixture of solution of sodium chloride and solution of ammonium hydrosulphide + 0.002 % Stearic acid/Toluene solution

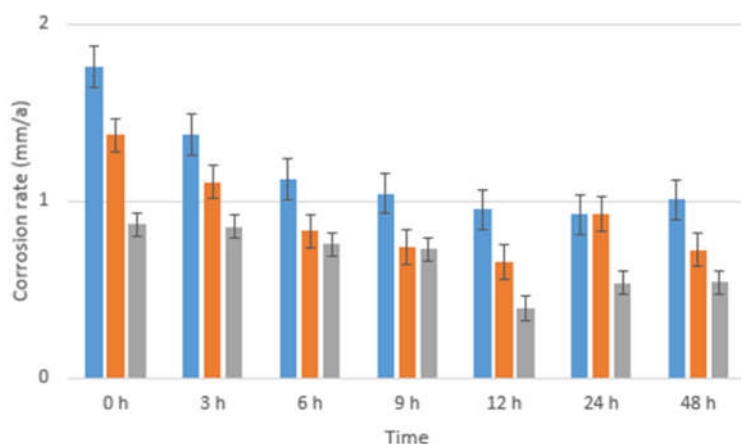


Fig.26. Averaged corrosion rates of ●=annealed, ●=carburized, ●=nitrided steel samples in a mixture of 3 % solution of sodium chloride and 3 % solution of ammonium hydrosulphide with 0.002 % stearic acid/toluene solution over time

Inhibitor efficiency of carburized steel in a mixture of 3% solution of sodium chloride and 3% solution of ammonium hydrosulphide ($t = 0$ h) with 0.002 % stearic acid/toluene solution is 21.96 % in relation to annealed steel, of nitrided steel is 50.70%.

In case of the mixture of 3% solution of sodium hydrosulphide and 3% solution of ammonium hydrosulphide in conjunction with the inhibitor “stearic acid/toluene”, the initial rate of corrosion across all kinds of steel samples (annealed, carburized and nitrided) did go down to somewhere between 1 and 2 mm/a, the nitrided steel samples showed the most effect of reduction in rate of corrosion, followed by the carburized samples and lastly the annealed samples.

The reduction in corrosion rate though was not very drastic across the samples.

It is also interesting to note that at ($t=9\text{h}$), the rate of corrosion for both nitrided as well as carburized samples were almost similar, although this behaviour was very briefly noted.

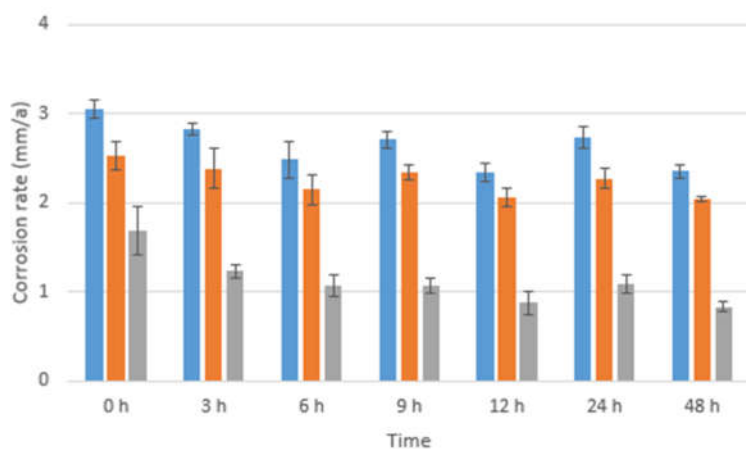
Once again, no measurement was possible using the LPR device in case of the mixture of 5% solution of sodium chloride and 5% solution of ammonium hydrosulphide even with the “stearic acid/toluene” inhibitor.

3.1.2. Comparison of corrosion rate of the pure technological condensate with added condensate

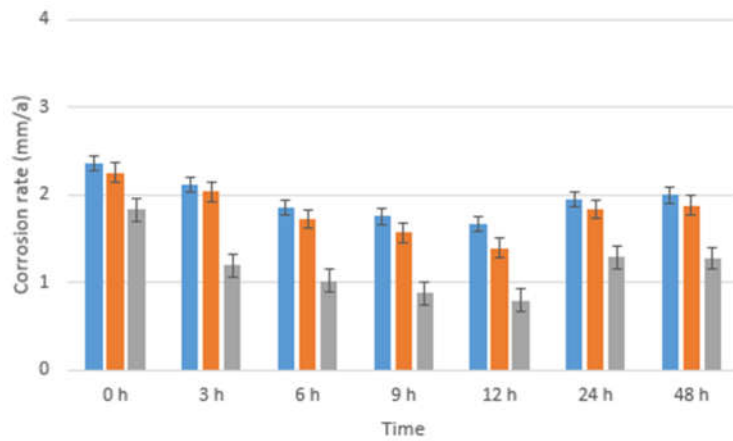
a) Inhibitor efficiency of carburized steel in technological condensate at initial state ($t = 0\text{ h}$) is 17.23 % in relation to annealed steel, of nitrided steel is 44.89%.

b) Inhibitor efficiency of carburized steel in technological condensate at initial state ($t = 0\text{ h}$) with 0.002 % Chimec 1839 is 4.29 % in relation to annealed steel, of nitrided steel is 22.26%.

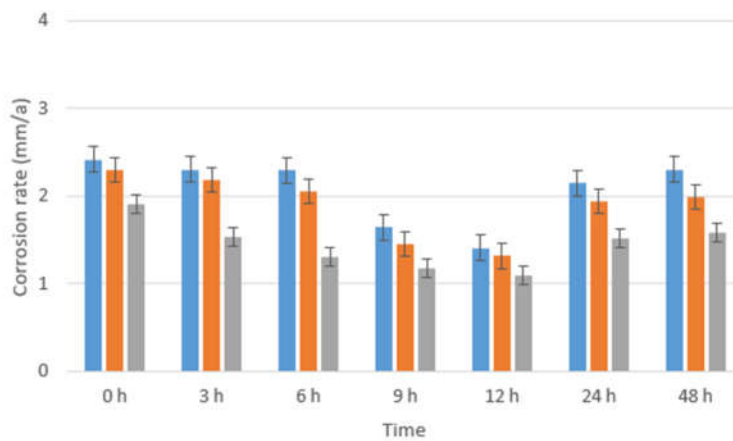
c) Inhibitor efficiency of carburized steel in technological condensate at initial state ($t = 0\text{ h}$) with 0.002 % Stearic acid/Toluene solution is 4.68 % in relation to annealed steel, of nitrided steel is 21.09%.



a) Technological condensate pure



b) Technological condensate with 0.002 % Chimec 1839



c) Technological condensate with 0.002 % stearic acid/toluene solution

Fig.27. Averaged corrosion rates of ●=annealed, ●=carburized, ●=nitrided steel samples in technological condensate over time

Although the rate of corrosion in case of technological condensate with both inhibitors (“Chimec 1839” as well as “stearic acid/toluene”) for all metal samples, i.e., annealed, carburized and nitrided samples, the trend of corrosion has not changed significantly.

In all cases of technological condensate as the aggressive media, the nitrided samples showed the least rate of corrosion, followed by the carburized samples and lastly the annealed samples.

From the data of table 6 it can be concluded that stearic acid has a similar effect as corrosion inhibitor on annealed steel. But the use of the inhibitors on surface hardened steels for ORLEN Lietuva is not advisable.

Table 6. Efficiency of the corrosion inhibitors Chimec1839 and stearic acid/toluene solution in relation to the electrolyte without inhibitors. The comparison can only be calculated for the same treated steel samples

Steel	Technological condensate with Chimec1839	Technological condensate with Stearic acid/Toluene solution
Annealed	22.96%	20.99%
Carburized	10.91%	9.01%
Nitrided	-8.68%	-13.15%

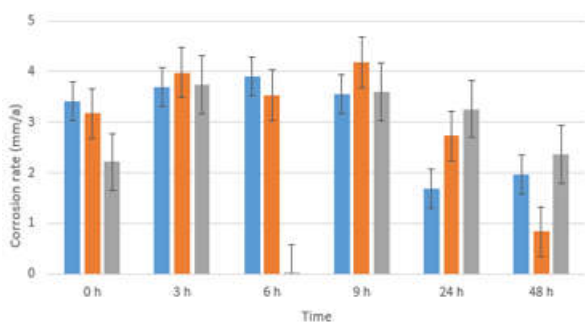
(Note: The negative sign of efficiency denotes the inefficiency and not actual mathematical meaning.)

3.1.3. Comparison of corrosion rate of the pure electrolytes with the technological condensate

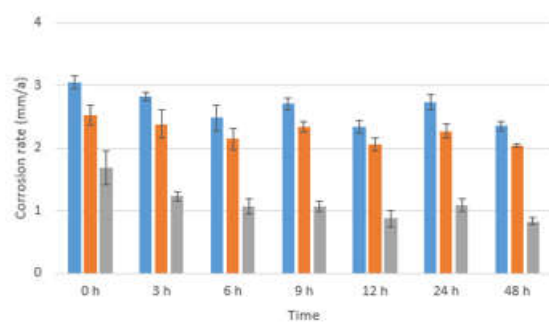
In this chapter and in following (3.1.4 and 3.1.5) the technological condensate is compared with the 5% solution. The concentrations of both electrolytes is nearly the same.

When compared to the 5% sodium chloride solution, the corrosion rate of all types of treated steel samples were more consistent and predictable under technological condensate. This was expected as the Technological condensate was made according to industry standards (usually regarded as gold standard for measurement amongst all these electrolytes).

Once again, in the technological condensate, the corrosion rate of nitrided steel samples were the least followed by the carburized samples and lastly the annealed samples.



a) 5% sodium chloride solution



b) Technological condensate pure

Fig.28. Averaged corrosion rates of ●=annealed, ●=carburized, ●=nitrided steel samples in different electrolytes over time

Surprisingly, the corrosion rate for carburized steel was shown to be quite high when compared to the nitrided and even annealed samples after 24h.

3.1.4. Comparison of corrosion rate of the electrolytes and the technological condensate each added with Chimec1839

Solution of sodium chloride + 0.002 % Chimec 1839 and solution of technological condensate + 0.002 % Chimec 1839

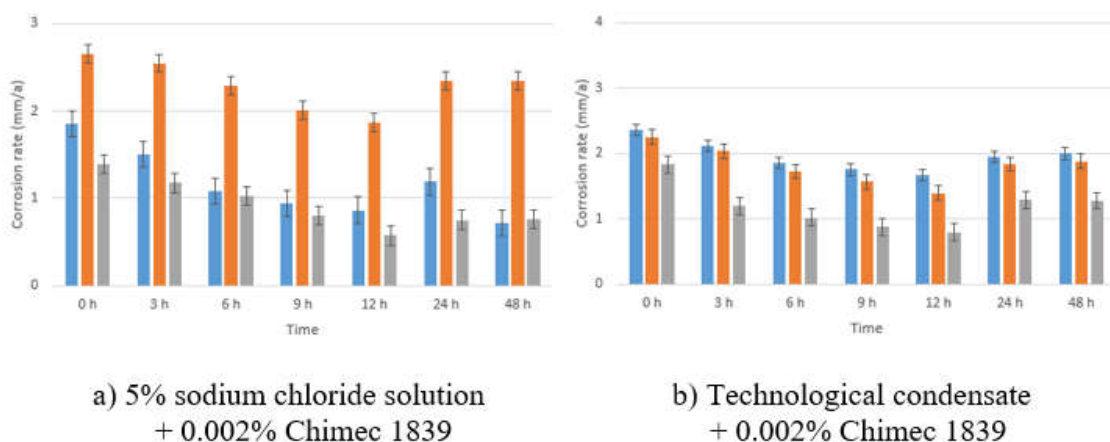


Fig.29. Average corrosion rates of ●=annealed, ●=carburized, ●=nitrided steel samples in different electrolytes over time

In the case of the 5% solution of sodium chloride with the Chimec 1839 inhibitor, the effect of the inhibitor, i.e., in reduction of the corrosion rate is much more pronounced and works significantly better at inhibiting the corrosion rate in nitrided and annealed samples than carburized samples.

The behaviour of Chimec on the corrosion rate on the metal samples differ when in presence of the technological condensate, as the rate of corrosion reduced across the samples but the inhibitive effect of Chimec on both the treated samples, i.e., nitrided as well as carburized samples were better than the annealed samples, with nitrided samples showing the most promising result consistently even when compared to the carburized samples. This goes on to indicate that nitrided steel samples in combination with the inhibitor Chimec works very well in Technological Condensate.

3.1.5. Comparison of corrosion rate of the electrolytes and the technological condensate each added with stearic acid dissolved in toluene

Solution of sodium chloride + 0.002 % Stearic acid/Toluene solution and solution of technological condensate + 0.002 % Stearic acid/Toluene solution

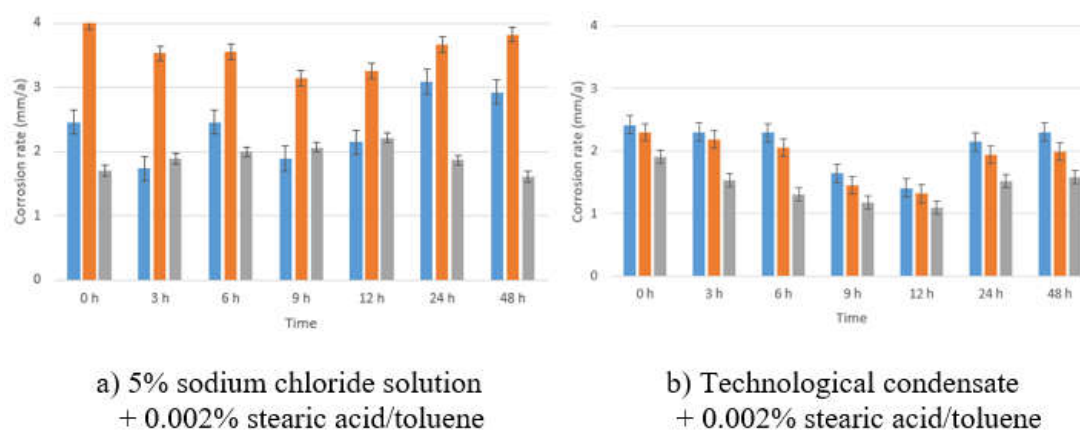
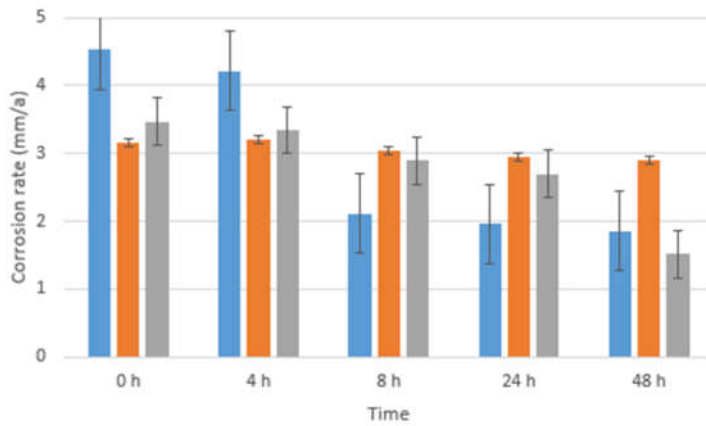


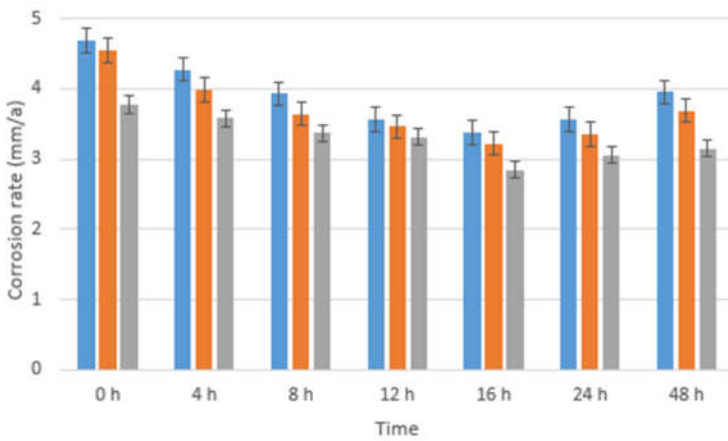
Fig.30. Averaged corrosion rates of ●=annealed, ●=carburized, ●=nitrided steel samples in different electrolytes over time

As expected of an inhibitor, the stearic acid/toluene mixture worked very well in inhibiting the process of corrosion in the technological condensate and the measurements showed that the inhibitor works better on surface treated samples, i.e., the carburized and nitrided samples than the annealed samples and out of the two surface treated samples, the inhibitor works best at reducing the rate of corrosion in the nitrided samples.

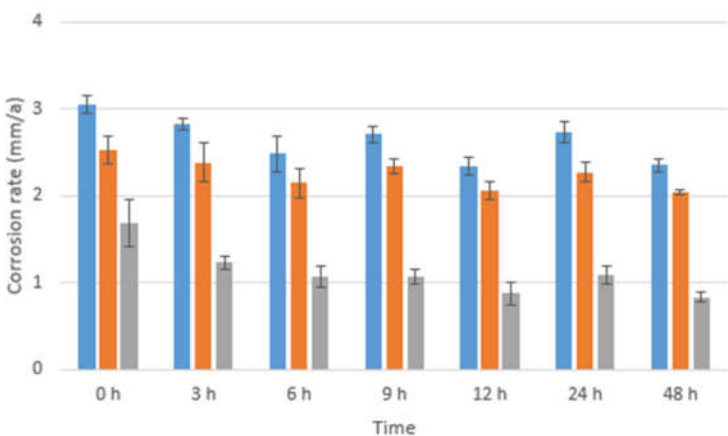
3.1.6. Comparison of corrosion rate of the pure 3% concentration electrolytes with technological condensate



a) 3 % solution of sodium chloride



b) 3 % solution of ammonium hydrosulphide



c) Technological condensate pure

Fig.31. Averaged corrosion rates of ●=annealed, ●=carburized, ●=nitrided steel samples in different electrolytes over time

Although at first glance, the corrosion rate across all kinds of samples under 3% ammonium hydrosulphide is seen as higher than that in 3% solution of sodium chloride, the trend of corrosion was more predictable and consistent in the ammonium hydrosulphide electrolyte.

When the corrosion rate of annealed, carburised and nitrided samples under 3% ammonium hydrosulphide solution and pure technological condensate is compared, in both cases, the rate of corrosion was highest in annealed samples. The corrosion rate in the surface treated samples were lower, with the nitrided samples showing better result than carburised samples.

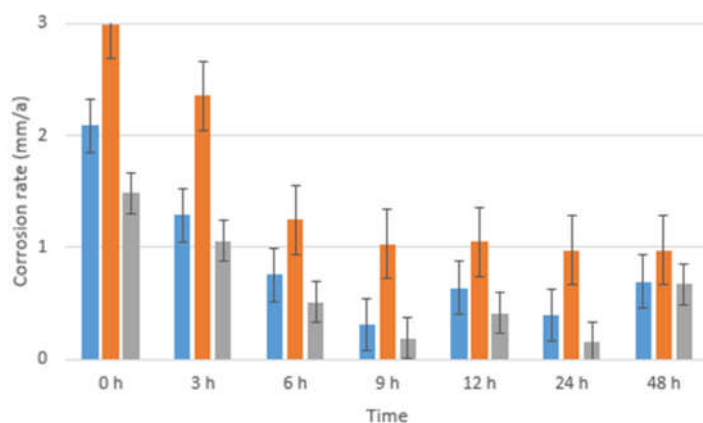
It must be noted that the corrosion rate in the pure technological condensate is much lower compared to that in the 3% sodium chloride electrolyte.

Table 7. Comparison of the corrosion rates at t = 0 h of the different steel samples in different pure electrolytes.

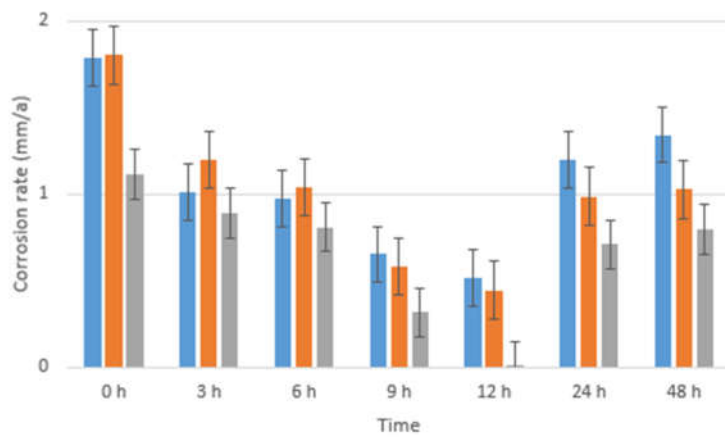
Steel	Corrosion rates in mm/a for 3% solution of sodium chloride	Corrosion rates in mm/a for 3% solution of ammonium hydrosulphide	Corrosion rates in mm/a for technological condensate pure
Annealed	4.54	4.70	3.05
Carburized	3.15	4.55	2.53
Nitrided	3.47	3.77	1.68

Without the use of corrosion inhibitors, the surface hardening of steel by nitriding increases the service life by a factor of approx. 1.8. The corrosion rate of nitrided steel in technological condensate is 1.68 mm per year which is the 1.8 part of 3.05 mm per year of annealed steel.

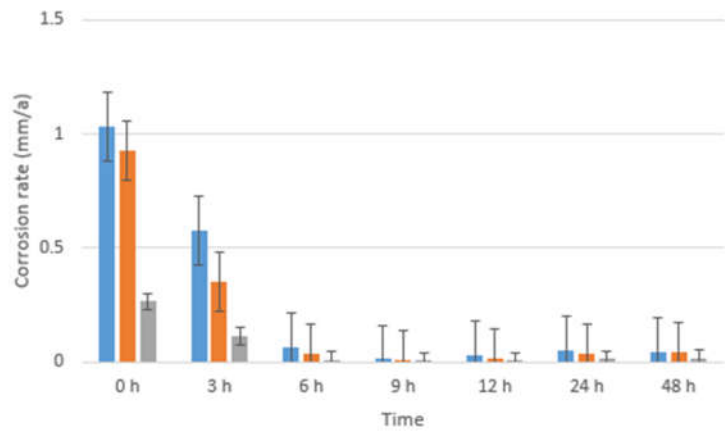
3.1.7. Comparison of corrosion rate of the pure 3% concentration electrolytes with technological condensate each added with Chimec1839



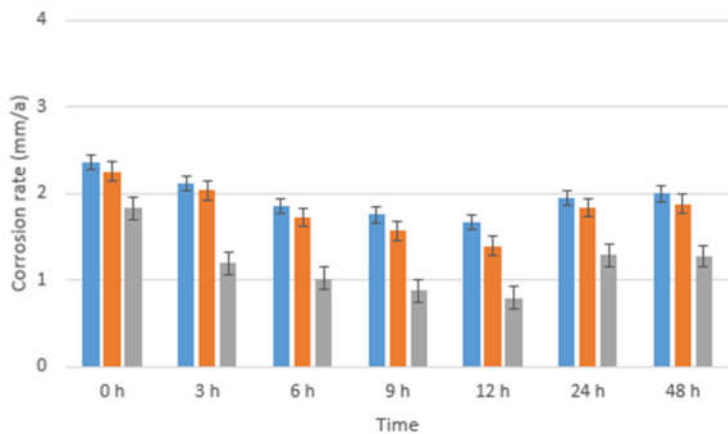
a) 3% solution of sodium chloride + 0.002% Chimec 1839



b) 3% solution of ammonium hydrosulphide + 0.002% Chimec 1839



c) Mixture of 3% sodium chloride and 3% ammonium hydrosulphide + 0.002% Chimec 1839



d) Technological condensate + 0.002 % Chimec 1839

Fig.32. Averaged corrosion rates of ●=annealed, ●=carburized, ●=nitrided steel samples in different electrolytes over time

In both cases of a) and b), the inhibitor Chimec 1839 has had an effect in reducing the rate of corrosion over time, but it must be noted that the trend of corrosion among the differently treated samples were not found to be similar.

The effectiveness of Chimec was found to be better in the case of 3% ammonium hydrosulphide than in 3% sodium chloride solution. The surface treated samples, especially the nitrided samples showed a promising reduction in the rate of corrosion than the annealed samples.

In case of c), a significant drop in rate of corrosion was noticed because of the inhibitor Chimec. In fact, the inhibitor worked really fast, right from the first measurement to the final one, consistently showing great reduction across the measurements and in all kinds of samples. The trend of corrosion and the effect of Chimec on the samples were found to be consistent, with the nitrided samples being the least, followed by carburised samples when it comes to the reduction in rate of corrosion over time. The annealed samples showed worser results compared to the rest of the samples.

In case of d), the Chimec showed consistent effect of reduction in corrosion rate with the most effect noticed on nitrided samples, followed by the carburised samples and at last the annealed samples.

Table 8. Comparison of the corrosion rates at $t = 0$ h of the different steel samples in different electrolytes in presence of the corrosion inhibitors Chimec1839.

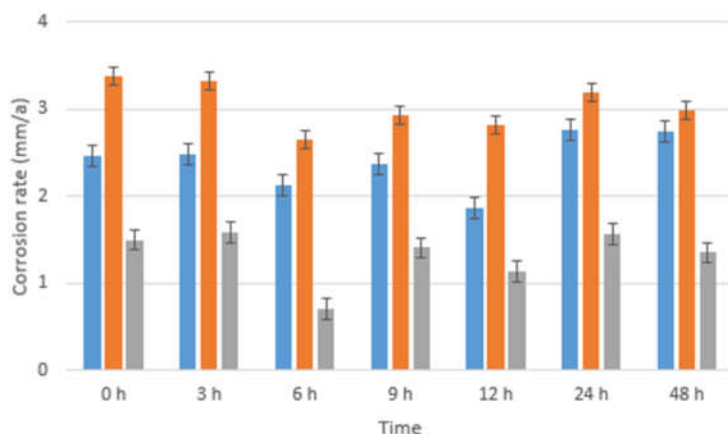
Steel	Corrosion rates in mm/a for 3% solution of sodium chloride + 0.002% Chimec 1839	Corrosion rates in mm/a for 3% solution of ammonium hydrosulphide + 0.002% Chimec 1839	Corrosion rates in mm/a for mixture of 3% sodium chloride and 3% ammonium hydrosulphide + 0.002% Chimec 1839	Corrosion rates in mm/a for technological condensate pure + 0.002 % Chimec 1839
Annealed	2.08	1.79	1.03	2.35
Carburized	2.99	1.80	0.93	2.25
Nitrided	1.49	1.11	0.27	1.82

The inhibitor efficiency of Chimec 1839 on nitrided steel in 3% sodium chloride and 3% ammonium hydrosulphide is 73.8 %, meanwhile the efficiency in technological condensate pure is only 22.6 %.

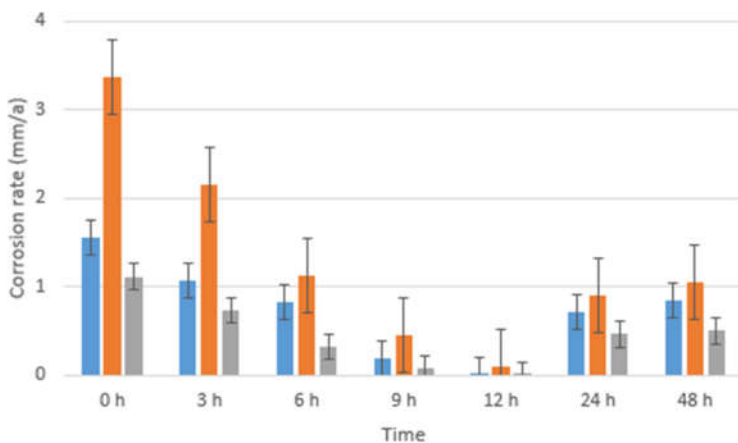
With the use of corrosion inhibitors, the surface hardening of structural steel in cases of pure electrolytes has a very huge advantage for extending the life time of chemical production plants until the factor of ca. 3.8. The corrosion rate of nitrided steel in the pure mixture of 3% sodium

chloride and 3% ammonium hydrosulphide is 0.27 mm per year which is the 3.8 part of 1.03 mm per year of annealed steel.

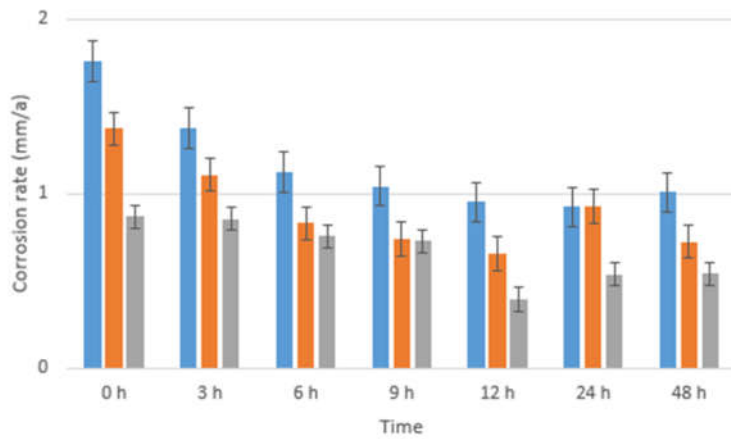
3.1.8. Comparison of corrosion rate of the pure 3% concentration electrolytes with technological condensate each added with stearic acid dissolved in toluene



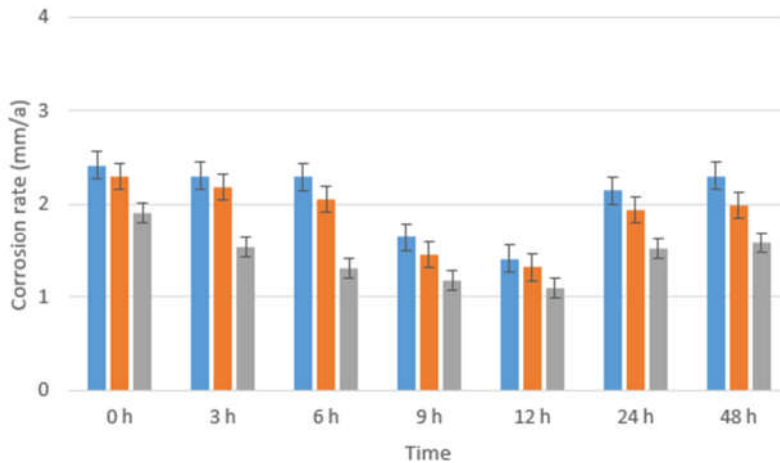
a) 3 % solution of sodium chloride + 0.002 % stearic acid/toluene



b) 3 % solution of ammonium hydrosulphide + 0.002 % stearic acid/toluene



c) Mixture of 3 % sodium chloride and 3 % ammonium hydrosulphide + 0.002 % stearic acid/toluene



d) Technological condensate + 0.002 % stearic acid/toluene

Fig.33. Averaged corrosion rates of ●=annealed, ●=carburized, ●=nitrided steel samples in different electrolytes over time

In terms of its composition, the Technological Condensate is best compared to the mixture of NaCl and NH₄SH. As can be seen from the comparison of the two column diagrams in Fig.33. c) and d) can recognize, the effect of the corrosion inhibitor in the Technological Condensate is partially canceled. The Technological Condensate presumably still contains production-related substances that are not present in the pure electrolytes.

The composition of all cations and anions of the salts contained in the technological condensate have to be determined to produce a model electrolyte.

Table 9. Comparison of the corrosion rates at t = 0 h of the different steel samples in different electrolytes in presence of the corrosion inhibitor stearic acid/toluene.

Steel	Corrosion rates in mm/a for 3% solution of sodium chloride + 0.002% stearic acid/toluene	Corrosion rates in mm/a for 3% solution of ammonium hydrosulphide + 0.002% stearic acid/toluene	Corrosion rates in mm/a for mixture of 3% sodium chloride and 3% ammonium hydrosulphide + 0.002% stearic acid/toluene	Corrosion rates in mm/a for technological condensate pure + 0.002 % stearic acid/toluene
Annealed	2.46	1.56	1.76	2.41
Carburized	3.38	3.36	1.37	2.30
Nitrided	1.50	1.11	0.87	1.90

3.2. Results of Vickers hardness values after every corrosion rate measurement

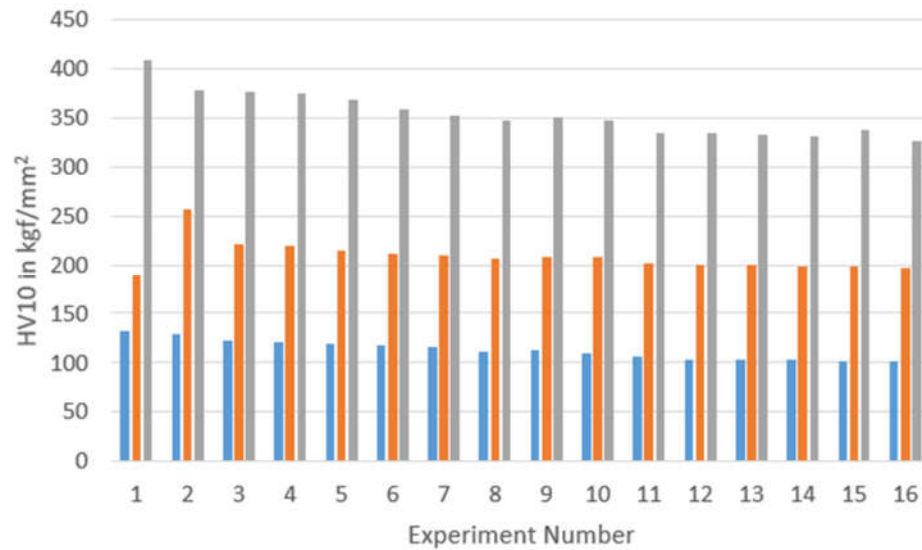


Fig.34. ●=annealed, ●= nitrided, ●= carburized steel samples

The decrease in hardness correlates with erosion of surfaces of the different surface treated steel samples. The biggest difference in hardness is shown in the case of carburized steel samples (49.87 kgf/mm² compared to 24.87 kgf/mm² of nitrided steel samples) which correlates very well with the experimental results.

In comparison with the literature (Scalera, 1993), the measurements showed the surface hardening of structural steel in most cases and in particular with a corrosion inhibitor, a positive effect on decreasing of corrosion in aggressive media was found.

It also shows that the types of surface hardening have an influence on the effectiveness of a corrosion inhibitor depending on its chemical properties.

The influence of the crude oil in aggressive media of industrial origin is unmistakable in comparison with the pure electrolytes produced in the laboratory. None of the “laboratory electrolytes” can fully explain the behavior of the technological condensate. Here, a complete analysis of the ionic components as well as the water-soluble components from the oil could provide the prerequisites for reproducing the corrosion behavior in the laboratory.

According to (Hernández-Espejel et. al., 2010), in the oil industry, especially worthy of note is a sour brine (NACE ID 182) commonly used to carried out corrosion studies and evaluation of corrosion inhibitors. NACE ID 182 contains a mixture as following: 1.64 M NaCl, 0.055 M CaCl₂, 0.018 M MgCl₂·6H₂O, 0.77 M CH₃COOH, 0.29 M Na₂S·9H₂O and 9.3×10^{-4} M Na₂SO₃ at pH 5.68 prepared from analytical grade reagents and deionized water (18.2 MΩ cm) .

POSSIBILITIES FOR FUTURE WORKS

For future work, the composition of the Technological Condensate should be analyzed in order to determine the components of salt and other components to explain completely the observed corrosion behavior of Technological Condensate, as for example the partially neutralization of the corrosion inhibitor.

In this work, the samples were freed from superficial adherence by grinding. This could probably be significantly improved by electropolishing. According to literature (Yang G. et al. 2017) electropolishing is also a way of reducing corrosion and has apparently not yet been investigated in connection with surface hardening. A superficial literature search on the Internet yielded no results.

In the interest of increased accuracy and a greater tolerance towards highly conductive electrolytes, the determination of the corrosion rate should be used with a potentiostat. In contrast to the measuring device used in this work, a potentiostat would also allow the determination of the corrosion potential in the form of Tafel plots. Tafel plots also allow further analysis, such as corrosion mechanism.

CONCLUSION

- In the case of the 3% solution of sodium chloride, the Chimec deteriorated the corrosion inhibition by 43.25% on carburized steel, while on the nitrided steel, the Chimec increased the inhibition by 28.70%. In the case of 5% solution of sodium chloride, the deterioration of the corrosion inhibition on the carburized steel is 0.28% less, while the inhibition on the nitrided steel is about 3% less than that of the 3% solution.

In general, "Chimec 1839" deteriorates the corrosion inhibition on carburized samples in sodium chloride solutions by approx. 43%, while on nitrided samples the inhibition is improved by approx. 28%.

- Inhibitor efficiency of carburized steel in 3% solution of sodium chloride and 3% solution of ammonium hydrosulphide at initial state with 0.002 % Chimec 1839 is 10.34 % in relation to annealed steel, of nitrided steel is 74.31%.

Obviously, in this case, the effect of "Chimec 1839" on the corrosion inhibition is very drastic.

- The corrosion inhibitor "Chimec 1839" works better than stearic acid in technological condensate, the difference is only approx. 1% in the case of carburized and annealed steel, while the difference in nitrided steel is approx. 5%.
- If Orlen Lietuva did not use any corrosion inhibitors, then surface hardening of the steel by nitriding increases the service life by a factor of approx. 1.8 would be worthwhile.
- In cases of pure electrolytes, the surface hardening of structural steel and using corrosion inhibitors has a very huge advantage for extending the life time of chemical production plants until the factor of ca. 3.8.
- The corrosion inhibitors work less effectively in technological condensate than in the mixture of 3% sodium chloride and 3% ammonium hydrosulphide prepared in lab. The inhibitor efficiency of Chimec 1839 on nitrided steel in 3% sodium chloride and 3% ammonium hydrosulphide is 73.8 %, meanwhile the efficiency in technological condensate pure is only 22.6 %. The technological condensate obviously contains substances that hampers the working of corrosion inhibitors.
- Nitriding is found to be the best hardening method because the loss of hardness over the period of thesis is found to be only the half of carburized steel samples (49.87 kgf/mm² compared to 24.87 kgf/mm² of nitrided steel samples).

- Stearic acid as corrosion inhibitor would be a good alternative to Chimec1839 for ORLEN Lietuva (technological condensate). Orlen could use waste oils based on vegetable oil (e.g. frying oil) instead of expensive commercial Chimec as an inhibitor to save costs. According to Glienskiene (Glienskiene L. 2018), ORLEN injects sodium hydroxide or ammonia water into the column during the rectification to neutralize acids. In the presence of the deep-frying oil, the sodium hydroxide solution split the esters into carboxyl acid as stearic acid.

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SUMMARY

Corrosion is an unavoidable problem in petroleum oil refinery industries due to the complicated work conditions such as high temperature, high pressure, pH value and ion concentrations in aggressive media. As the main construction material for equipment in oil, gas and petroleum industries is steel due to his availability, and low cost.

The properties of numerous metals and alloys rely upon the condition of its surface layer. Strengthening (hardening) this layer can further improve the mechanical properties of the material. Thermochemical treatment is a process of saturating the surface layers of metals with one or more elements that alter the chemical composition of the surface layer and get the desired surface properties and microstructure. Thermo-chemical treatment of metal increases its resistance to abrasion and environmental effects (corrosion, high-temperature oxidation, acids).

One of the most known methods to reliably yet cost effectively protect metals from corrosion in oil and gas pipelines is the use of organic inhibitors.

In this work, thermal-chemical surface hardening nitriding and carburizing –hardening to increase the corrosion resistance of steel was performed. This was done by measuring the corrosion rate of the various samples in different electrolytes. Additionally, the effect of corrosion inhibitors were also tested.

Generally, the commercial inhibitor "Chimec 1839" deteriorates the corrosion inhibition on carburized samples in sodium chloride solutions while on nitrided samples the inhibition is improved. Stearic acid as corrosion inhibitor would be a good alternative to Chimec1839 as it is cheaper.

Furthermore, it is not possible to deduce the corrosion rates in technological condensates from the measured data of corrosion rates of hardened steel samples in pure electrolytes.

The experimental results from linear polarization resistance technique have shown that corrosion resistance provided by nitriding to be the best.

Keywords: steel S235, corrosion inhibitor, linear polarization resistance technique, condensate treatment block, carburizing–hardening, nitriding .