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CORROSION, CORROSION PREVENTION & SOLUTIONS IN SYSTEM OF PIPELINES

Thesis

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ABSTRACT

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Pipeline system is used in almost every industrial activities: they transport materials and waste, including fluids such as water, liquid chemicals; or gases and steam, from and to different stages of an industrial cycle. For pipelines which are made of metal, one problem of consideration is corrosion. The corrosion inside pipelines may seriously affect quality of the substance they transport (for example: heavy metals in drinking water); or the construction of the system itself. This thesis discusses the corrosion phenomenon, especially in systems that transport water, as well as studies the practical data to get a better understanding of it.

The complete thesis is supposed to present clear, detailed, and accurate knowledge about corrosion related issues in water transporting system. It is divided into two parts: theoretical and practical. In the theoretical part, the subject of corrosion principles is discussed, as well as the types of corrosions; how they affect the efficiency of different industries and what are the solutions for them. The information for this part will be taken from literature, books and other reliable references; most of which focuses on systems that transport water. In the practical part, several experiments were conducted. The results of mentioned experiments were analysed using mechanical/chemical methodology and calculations. By the evaluation of mentioned data, corrosion is understood better in a practical perspective.

Key words
Corrosion, corrosion rate, material selection, pipelines.

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1 INTRODUCTION

Piping system may be one of the most common engineering structures, which presents in various aspects of daily life. It is not often that a boiler, or an extraction column is seen; but pipelines can be observed in many places: from private households, public locations such as schools or restaurant, to industrial warehouses and processing areas. Pipelines serve different purposes, like carrying drinking water to household and taking out waste water; transporting working fluids for heat exchangers; and providing necessary materials for industrial processes. Because they play such an important role, it is essential that when design a piping system, engineers should consider various factors, but most importantly, the costs of building and maintenance; along with the duration of pipelines.

For pipelines made out of metallic materials, corrosion is a serious and continuous threat to their duration as well as maintenance costs. Corrosion occurs when the metal reacts with different environmental factors, forming numerous substances from the original metal which leads to the worn out of material. The costs of refinery can be significant, and in some cases, it can result in other severe issues (for example, contaminants in drinking water if there is corrosion inside a pipe). Since every kind of pipeline has to interact somehow with the environment out and inside them, corrosion is inevitable. The situation is more serious in the industrial zone, because the concentration of reactive chemicals is higher.

Although corrosion cannot be stopped, there are still many methods to minimise the negative impacts of this phenomenon. In this thesis, corrosion will be discussed in details - its principles, types and effects; mostly focusing on pipeline corrosion when liquid substances are present. The thesis will, moreover, include ideas of solving corrosion problems, especially solutions for industrial pipeline systems. For the practical work, corrosion rate method will be used. Corrosion rate (corrosion/time) is a unit used to measure the lost of metal due to corrosion in an amount of time. By testing the corrosion rate of different pipe metals in different liquid environments, the data can be analysed and evaluated to conclude why choosing the right materials for constructing pipelines is important to fight against corrosion. Some other data from books and reliable resources will also be analysed and compared to the experimental data, in order to interpret the issues in accurate perspectives.

2 THEORY

This section focuses on theoretical background about corrosion and related issues. It involves issues such as corrosion's mechanism, its definition, and types. The section also includes some case study in which corrosion occurred in reality and their impact. The solutions for corrosion and preventing methods are also mentioned. Since this section focuses mostly on theoretical study, practical data is also discussed, but not in great detail. Most of the theories will focus on corrosion in liquid environment.

2.1 Definition & Principles

Corrosion is the gradual damage to metal when it interacts with the environment around. Most types of environment are corrosive: water, soil, liquid/gaseous chemicals, or just air. Those are common environments that metal structures are located, but in fact; almost anything that comes in contact with the metal like orange juice, alcohol, or even blood and body fluid (in case of medical implants) could be the environment of corrosion. This phenomenon is easy to observe in daily life, as it occurs frequently: yellow stains on the kitchen sink, brown rust on old cars, or copper jewellery which had been worn for a long time starts gaining green marks. Even the Statue of Liberty is the victim of corrosion. Almost every structure made of metal can be corroded (Fontana & Greene 1983). Picture 1 shows the Mannerheim statue located in Finland, and its dark-couloured patches due to corrosion.

Picture 1: Mannerheim Statue, Finland (Annie 2013)

While corrosion seems to be quite a common issue, it is complicated and inevitable. The situation is more serious in industrial plants, where there are all kinds of liquid, gaseous, organic and inorganic chemicals, which react easily to metal and are potential corrodents. Moreover, all industrial plants should have a piping system build, either to transport materials and waste; or for other purposes like heating, cooling, or carrying steams. These pipelines are complex structure and if they are made of metal, corrosion will most likely occur. (Fontana & Greene 1983.)

Picture 2: A corroded pipe (Dicoot 2017)

Picture 2 shows a pipe which had been completely destroy by corrosion. The brownish metal oxides is the product of reactions between the pipe and its surroundings. As it can be seen from the picture, there is a large crack on the metal surface. If there is no prevention or refinery against corrosion, the metal will be gradually consumed in the reaction, which leads to loss of material and eventually the crack. It would be a serious problem if this pipe was transporting oil, or harmful chemicals, as it can cause an environmental disaster. (Bradford 1993.)

Indeed, other materials (plastic, ceramic, or glass) can as well be damaged by the environment. The destruction of ceramic, glass and polymer materials, as they react to their surroundings, is also considered corrosion. However, the principle of these corrosion types are quite different from metals. In this thesis, only corrosion in metals will be discussed. All metal share the same basic corrosion mechanism which will be examined further in this section. (Fontana & Greene 1983.) Corrosion is the result of chemical reactions. Metal interacts with the environment, forming more chem- ical stable substances. These stables can be, for example, metal oxides, sulphides, or hydroxides. The corrosion of iron and steels are a specific type known as ferrous corrosion. (Bradford 1993; Schweitzer 2010.)

Based on the environment that metal reacts with corrosion can occur in two ways: dry and wet corrosion. Dry corrosion (dry oxidation) takes place without the presence of moisture or water in the environment; while wet corrosion means the metal has some kinds of contact to aqueous substance(s). The affect of dry/wet environment can change the situation significantly. (Spruck 2018.)

2.1.1 Dry corrosion (Dry oxidation)

In most of dry corrosion cases, the metal interacts with oxygen in the atmospheric air. Except for silver and gold, which are not very reactive, all other metals can react with air forming metal oxides. For M is ”metal”, the reaction with oxygen can be written as:

$$M + O \longrightarrow MO$$
$$M \longrightarrow M^{2+} + 2\,e$$
$$O + 2\,e^{-} \longrightarrow O^{2-}$$

Or, to be more general:

$$M \longrightarrow M^{n+} + n \cdot e^{-}$$

In the progress, the metal M loses some electrons and becomes an ion. This metal ion comes in contact with oxygen in the air, reacts and forms metal oxides. As a result of this reaction, a layer of metal oxide MO is formed on top of the metal (Spruck 2018). When the reaction occurs, there are three possible situations, which are shown in Figure 1:

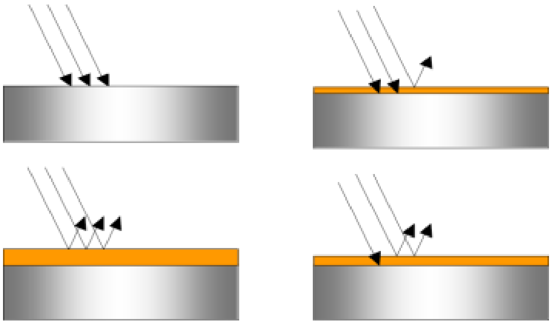


Figure 1: Three types of oxidation layers (UNSW Sydney 2013)

The first scenario shows fresh, untouched metal exposed to the atmospheric air. Eventually, corrosion takes place and forms metal oxide, a yellowish layer. Now in the picture located at the top right corner, first possible outcome can be observed: The metal oxide layer is thinner than the metal layer. In this case, as corrosion products are often quite brittle, the metal oxide layer will most likely crack open, and the metal ion M^{n+} will diffuse outwards, while oxygen ions flow inward and continue the corrosion progress. (Spruck 2018.)

The second scenario is that, corrosion occurs rapidly, which results in higher volume of the metal oxide than the actual metal (picture at the bottom right corner). For this case, the metal oxide will wrinkle and spring away, consequently leading to more exposing of fresh metal. When the volume of metal oxide formed matches volume of metal $V_{MO} = V_M$, it could be a positive scenario (picture at bottom left corner). Since this metal oxide cannot react further with oxygen in the air, it will act as a ”coating” that protects the metal below from corrosion. (Spruck 2018.)

Sometimes, dry corrosion is accepted and encouraged. The reason is that it forms a protective layer, rather than leaving the fresh metal exposed to corrosion factors. This phenomenon is called passivation, and the corrosion rate could be reduced by it. However, the efficiency of this protective layer in fact depends on the type of material (UNSW Sydney 2013). For example, Figure 2 shows the differences between aluminium and magnesium metal:

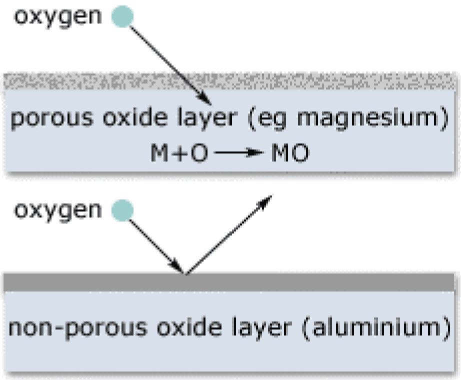


Figure 2: Passivating layers of different metals (UNSW Sydney 2013)

Magnesium forms porous oxide layer(s) when reacts to atmospheric air, so oxygen can still go inside these pores and corrode the metal further. Aluminium, on the contrary, forms continuous layer which can effectively protect the material from corrosion. This is the reason why choosing the right material is really important when it comes to corrosion prevention. Some metals can be modified so that they are able to create this protective layer. For example, chromium and nickel in stainless steel helps forming passivation layer (UNSW Sydney 2013).

Another aspect to consider about dry corrosion is that it is heat sensitive. Normally, dry corrosion occurs at ambient temperature. When high temperature is involved, the electrons within one metal can move faster, and the corrosion rate increases. In pipeline systems, dry corrosion often takes place on the outer layer of a pipe. Although it could lead to cracks, pits and eventually liquid leakage, dry corrosion does not affect the material transfer within a pipe. Pipelines which are located in high temperature areas have higher chances to suffer corrosion, and the consequences are also much more serious. (Chaturvedi 2015.)

Besides dry oxidation, there are other two types of dry corrosion: liquid metal corrosion and anhydrous liquid corrosion. Since only corrosion of pipelines is focused, these two situations can be skipped, for that they rarely occur within a pipeline system, but rather in boilers, reactors and/or other parts of an industrial plant. (Chaturvedi 2015.)

2.1.2 Wet corrosion

When corrosion takes place in wet environment, the situation gets much more complicated. In liquid transporting pipelines, there are always liquid inside a pipe, therefore wet corrosion is almost inevitable.

Wet corrosion can also occur outside a pipe when the environment is affected by moisture factors, for example, rain. It is, in fact, the most common type of corrosion (UNSW Sydney 2013). Both dry and wet corrosion are chemical reactions, but in the wet corrosion case, it is essentially elec- trochemical. As the name suggests, this progress involves the generation of a voltage and, some kind of electrical connections between an anode and a cathode. As a matter of fact, this is called a ”corrosion cell”. Figure 3 describes a typical corrosion cell. (Lewis 2014.)

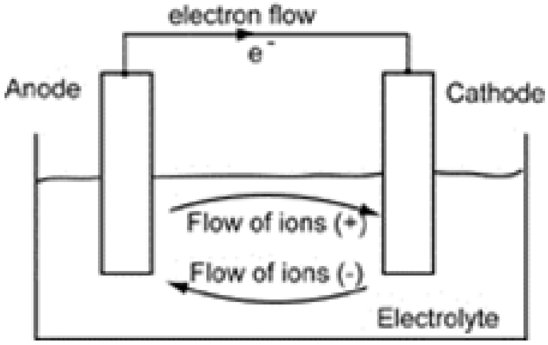


Figure 3: A corrosion cell (Lewis 2014)

A corrosion cell, or electrochemical cell, consists of four compulsory elements. Those are (1) The anode: This is our metal M, which is corroding. It gives out electrons to the environments and becomes metal ions; (2) The cathode: Discharged electrons from the anode moves to the cathode, at which they can react with other elements; (3) Electron flow/Electrical connection: For the reaction to take place, it is necessary for the anode and cathode to have some kind of connection. It can be direct physical contact, or a wire. Because electrons cannot go directly into the electrolyte, they will flow along this connection; and (4) Electrolyte: The liquid environment. (Lewis 2014.) If corrosion takes place, there must be the presence of all four elements mentioned above. If one element is not present, the electrochemical reaction will stop and so does corrosion. The anode and cathode, in many cases, are located on the same piece of metal. (Bradford 1993.) To give a clearer idea about this phenomenon, some examples below can be evaluated. By analysing how each element work in a corrosion cell, its mechanism could be understood better. Below this section is Figure 4, which shows the wet corrosion progress of steel. (Patel 2017.)

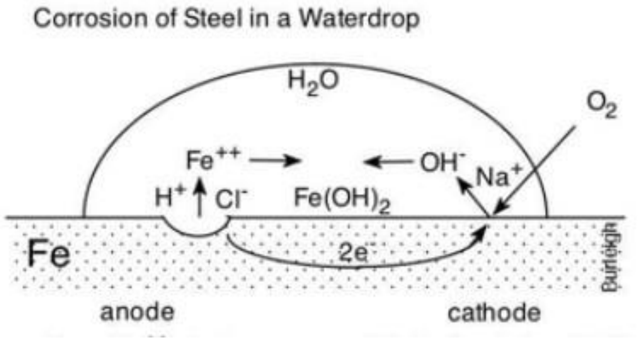


Figure 4: The corrosion of steel in water (Patel 2017)

In the figure, the four elements of an electrochemical cell are presented: the anode (1) and cathode (2) both located on the metal steel surface; water acts as electrolyte (3); and since the anode and cathode are the same piece of steel, thet have a physical electrical connection (4). It should be noted that water conducts electricity, and that is why it can act as a conductor for electron flows. Because steel is an alloy of iron, it is possible to assume for this reaction, that the metal M is Fe. Now, it is necessary to think about what kind of reactions is happening in this corrosion cell. In the previous section, it had been discussed that the general reaction is written as (Deziel 2018):

$$M -\longrightarrow M^{n+} + n \cdot e^{-}$$

So, with steel as the anode, the reaction is:

$$Fe -\longrightarrow Fe^{2+} + 2\ e^{-}$$

This is called the anode reaction, in which the anode gives out electrons as it corrodes. These electrons, however, do not go out directly to the environment to react as in dry corrosion; but rather move along the piece of metal until it reaches the cathode, where the next reaction takes place. This happens because at low voltage, electrons cannot pass through the electrolyte. (Deziel 2018.)

The reactions at the cathode are called cathode reactions. Since there is only one type of metal that corrodes, but different in corrosive environments, it is possible that there are more than one cathode reaction. In the steel verus water case, water is treated as a reactant. Water contains dissolved oxygen, so it can consume electrons from the anode to form hydroxide anion according to the reaction below. (Deziel 2018):

$$O_2 + 2\ H_2O + 4\ e^{-} -\longrightarrow 4\ OH^{-}$$

Eventually, the metal cations will meet the flow of hydroxide anions, and react with each other:

$$Fe^{2+} + 2\ OH^{-} -\longrightarrow Fe(OH)_2 + 2\ H^{+}$$

Aside by the part that reacts with the discharged electrons from the cathode, water H_2O itself has the ion $H^+(aq)$ and $O_2(aq)$. These elements can react with the metal Fe^{2+} which are formed in the anode reaction:

$$4\,Fe^{2+}(aq) + 4\,H^+ + O_2 \longrightarrow 4\,Fe^{3+}(aq) + 2\,H_2O(l)$$

The above reaction produces water and iron (III) ion Fe^{3+}. This ion, consequently, goes on and reacts with the hydroxide anion OH^-, forming iron (III) hydroxide:

$$Fe^{3+}(aq) + 3\,OH^-(aq) \longrightarrow Fe(OH)_3$$

When being dehydrated, the compound turns into $Fe_2O_3 \cdot H_2O$, which is also known as rust (Deziel 2018).

Conclusively, it is safe to say that the material and products of wet corrosion progress are almost the same as dry corrosion, but its mechanism and stages are much more complicated. Especially with this example, in which there are only one metal (steel) and water as the corrosive environment. It also shows that even something simple as a pipe transporting water is at risk of corrosion, let alone other liquid chemicals such as acids or working fluids. In chemical plant particularly, the situation can get much more severe and complicated, since there is the presence of organic liquid, and their corrosion reactions with metal will not be as simple as steel and water. The addition of high temperature and pollutants in air could also make corrosion worse. (Fontana & Green 1983; Bradford 1993.)

Another point is that, in the previous example, there is only one metal that act both as an anode and cathode. In liquid transporting pipe, the inside of the pipe is usually made by one united metal, therefore the example makes sense. But outside of the pipe system, due to design factors, there could be cases when there are two metals present. For that instance, it should be decided what metal will corrode to make suitable design. (Fontana & Green 1983; Bradford 1993.) This is quite an issue of interest, and it will be discussed more thoroughly in section 2.4 Prevention & Solutions.

In conclusion, corrosion mechanism is the chemical reactions of metal material and its surrounding environment. Dry corrosion occur without moisture presence, and wet corrosion takes place in aqueous environment. Wet corrosion is electrochemical process, which happens inside an electrochemical cell. Both wet and dry corrosion involves ion exchange between the metal and environmental reactants. (Fontana & Green 1983; Bradford 1993.)

2.2 Corrosion Types

By its definition and mechanism, it can be seen that corrosion is a really complicated process. It can develop in many directions for just one metal, depending on its surrounding environments. Hence, studying and evaluating different types of corrosion is also a complex task. There are various ways of classification that were discussed among engineers, and it is not easy to tell what is right and the most suitable. Thus, in this thesis, only the most common system of classification will be discussed, which is widely accepted and frequently used with slight modifications. (NACE International 2017.)

In 1967, Fontana & Greene mentioned this classification system within their book ”Corrosion Engineering”. Based on the way corrosion attacks and deforms a metal, it can be classified into eight types. Each type of corrosion will be discussed thoroughly in this section. (Fontana & Greene 1983).

2.2.1 Uniform Attack

According to Fontana and Greene (1983), uniform attack may be the most typical type of corrosion. It is also known as uniform corrosion. Uniform attack can occur in both wet and dry conditions. When this form takes place, it damages the exposed metal surface, as the name suggests, uniformly. Pipes or other metal structure suffers uniform attack can be observed with large brownish rust patches all over their surface.

Picture 3: Uniform corrosion (Bardi, 2019)

Picture 3 presents what uniform corrosion looks like. Rust spreads evenly on the metal surface, but as it can be observed from the picture, it only creates a thin layer with no greater damage. No pits, cracks or crevices as shown in Figure 2. In fact, this type of corrosion is quite favourable to engineers. Since material is attacked uniformly, by the loss of metal, a concept of corrosion rate can be determined. This rate tells us how much material (usually measured in thickness or weight) is lost to corrosion in a period of time. (Fontana & Greene 1983.)

By obtaining this corrosion rate, engineers can decide how severe the situation will get, and propose reasonable solutions. The standards for corrosion rate, in fact, depends on many different factors.

Sometimes the same rate is unacceptable for one plant, but convenient enough for other with, for example; shorter economic lifespan. (Spruck 2018.) Corrosion rate will be discussed further in section 2.4 Prevention & Solutions and 3 Practical Research.

2.2.2 Galvanic Corrosion

Galvanic corrosion is also known as two-metal corrosion; or contact corrosion. Its name comes from the fact that galvanic corrosion involves two dissimilar metals, which have a physical or electrical contact to each other. This is an electrochemical process, so it also requires the presence of and electrolyte. In some cases, it is not necessary for the electrolyte to touch both metals, but only one of them. (Fontana & Green 1983.)

Picture 4: Galvanic corrosion (Belmont, 2018)

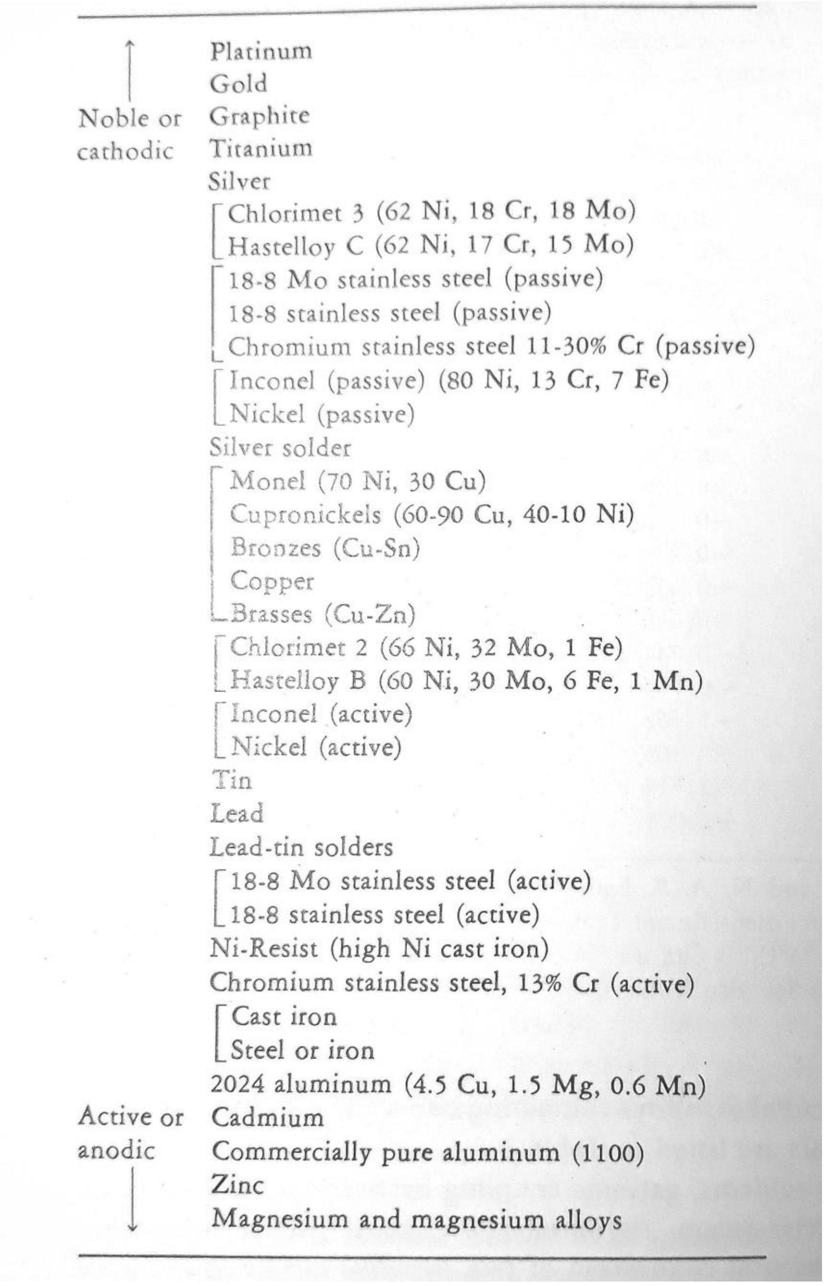
In engineering design, it is not rare to see different metals come in contact with each other. Picture 4 shows a case of galvanic corrosion between a metal surface and the screws located on it. These two metals form a ”galvanic couple”, in which one acts as the anode and the other as the cathode. Refer to the corrosion/electrical cell which has been discussed before, when corrosion takes place, the anode is damaged while the cathode is not. It would be the same case with galvanic corrosion. The metal which is less resistant to corrosion becomes the anode and is damaged significantly; at higher rate compared to when it stands alone with no contact. Meanwhile the other one, with higher resistance, takes lesser corrosion damage. (Fontana & Greene 1983.)

When design an engineering structure with two metals contacting each other, it is necessary to think of galvanic corrosion, and determine which of the two will become an anode. This means that it would be unfavourable for pipelines to corrode rapidly, while the screws keeping them together suffers very little or almost no corrosion. Hence, to know exactly what metal will be corroded, it is necessary to examine further into the characteristics of metals, and how they will behave in certain situation. In this case, the electrode potential of metal should be discussed. If a metal in galvanic corrosion becomes the cathode, it has higher reduction potential E^0. In other words, the higher the E^0 value, the more resistant to corrosion.

E^0 value of metals can be looked up in database or books. (Fontana & Greene 1983.) For example, according to the database from Weast, 1988; if copper and silver are placed in contact with each other and submerged into an electrolyte, copper will be corroded first because it has lower E^0 value and is more reactive. (Bradford 1993.)

In reality, when building pipelines, elemental metals are rarely used, but their metallic alloys. It will be more suitable if a galvanic series of electrode potential is considered. This galvanic series is quite the same as the reduction potential series, but it lists common alloys that are used widely in commercial engineering. Table 1 below shows us a galvanic series of metals and alloys in seawater. (Fontana & Green 1983.)

Table 1: Galvanic series of some metals in sea water (Fontana & Greene 1983)



↑
Noble or cathodic

Platinum
Gold
Graphite
Titanium
Silver
Chlorimet 3 (62 Ni, 18 Cr, 18 Mo)
Hastelloy C (62 Ni, 17 Cr, 15 Mo)
18-8 Mo stainless steel (passive)
18-8 stainless steel (passive)
Chromium stainless steel 11-30% Cr (passive)
Inconel (passive) (80 Ni, 13 Cr, 7 Fe)
Nickel (passive)
Silver solder
Monel (70 Ni, 30 Cu)
Cupronickels (60-90 Cu, 40-10 Ni)
Bronzes (Cu-Sn)
Copper
Brasses (Cu-Zn)
Chlorimet 2 (66 Ni, 32 Mo, 1 Fe)
Hastelloy B (60 Ni, 30 Mo, 6 Fe, 1 Mn)
Inconel (active)
Nickel (active)
Tin
Lead
Lead-tin solders
18-8 Mo stainless steel (active)
18-8 stainless steel (active)
Ni-Resist (high Ni cast iron)
Chromium stainless steel, 13% Cr (active)
Cast iron
Steel or iron
2024 aluminum (4.5 Cu, 1.5 Mg, 0.6 Mn)
Cadmium
Commercially pure aluminum (1100)
Zinc
Magnesium and magnesium alloys

Active or anodic
↓

As it can be seen from the table above, platinum is the most noble metal and has highest corrosion resistance; while magnesium is the most likely to suffer corrosion. So when it comes to galvanic corrosion, the galvanic series could be considered to choose the material wisely. For example, if a system of steel pipelines is designed to run under seawater, it is probably not sufficient to have pipe holders/screws made of nickel. It is the same case for valve stems, or shafts of pumps on the pipeline: if they are made of, for instance, stainless steel, then it is not reasonable to have them packed with graphite. The environment surround galvanic couple also plays an important role, so it is essential to examine the potential series in the correct conditions. To conclude, galvanic corrosion is almost inevitable when design a structure which has two metal contact, but it can be reduced by studying metal behaviour & choosing the right metal. (Fontana & Green 1983.)

2.2.3 Crevice Corrosion

Crevice corrosion, as the name suggests, attacks metal area inside gaps and crevices. These could be the cramped spaces between mechanical parts of pipes, joints and junctions; or the area under bolts and rivets. They could also be narrow holes or cracks which tends to deposit small volume of working fluids/solutions. Eventually, these aqueous volume becomes the corrosive environment. Because of this, crevice corrosion is also called gasket or deposit corrosion (Fontana & Greene 1983).

Picture 5: Crevice corrosion (Nanan 2018)

Picture 5 shows the result of crevice corrosion under a bolt’s head. The mechanism of crevice corrosion is quite the same with the electrochemical case, but with the lack of oxygen in the later stage of corrosion. To understand more about this, take an example of a piece of metal M submerged under seawater. At first, the reactions occur quite similar to the steel and water example which has been discussed in Section

2.1. Metal M gives out electrons and oxygen is reduced as (Fontana & Green 1983):

$$M \longrightarrow M^+ + e^-$$
$$O_2 + H_2O + 4\,e \longrightarrow 4\,OH^-$$

At the first stage of crevice corrosion, electrochemical reactions take place normally. Metal M is corroded in uniform with the same mechanism as steel in water. However, since the crevice has very small space and therefore bad convention, the oxygen amount inside it starts decreasing. This is when crevice corrosion enters its second stage, oxygen depletion. (Fontana & Green 1983.)

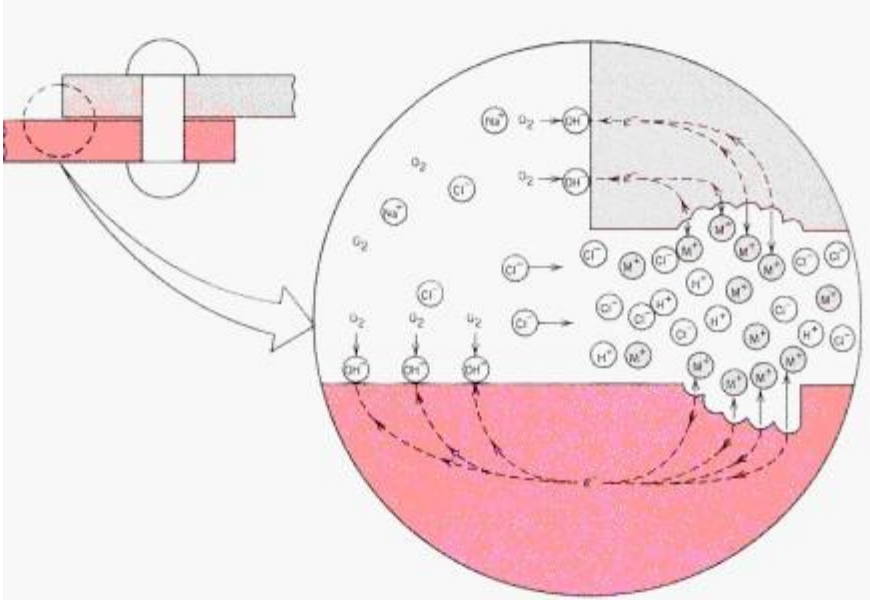


Figure 5: Crevice corrosion - second stage (Willey 2000)

Figure 5 shows what happens in the second crevice corrosion stage. At this stage, the oxygen level inside the crevice had decreased significantly. This will lead to the reduction of anion OH^- and eventually, the increasing of metal M^+ cations. The excess number of cations cause charge imbalance in the crack, and to balance it, negative ion Cl^- inside seawater starts flowing in. The crevice metal now suffers severe corrosion, first because the rate of M^+ ion generation had increased. Moreover, with the exception only to alkali metals, most metal salts hydrolyse in water. It is expressed by the equation below (Fontana & Green 1983):

$$M^+Cl^- + H_2O \longrightarrow MOH + H^+Cl^-$$

Therefore, not only the Cl^- ions react with M^+, but it also interact further with water and form acidic solution. The pH level is thus, reduced even more, and the environment becomes really corrosive. Corrosion rate is consequently accelerated. (Fontana & Green 1983.)

2.2.4 Pitting

Pitting attacks exposed metal and forms pits (holes that go deep into the metal thickness). Contracted to uniform attack which occurs evenly all over the metal surface, pitting only forms holes in some areas. Holes resulted from pitting have various diameter measurements, which usually equal to their depth. Sometimes pits can be quite large, but in most of the case, they are relatively small. These small pits may form close together creating bigger pits and increase the damage. (Fontana & Green 1983).

Picture 6: Pitting corrosion (Willey 2018)

Picture 6 presents a real life example of pitting. It can be seen that some pits are right next to each other, forming a bigger one; and some just locate randomly on the metal piece. Pitting may be one of the most annoying form of corrosion, since it attacks randomly, rapidly; and takes time to show itself. The pits formed tend to develop in the direction of gravity. That being said, most pits will pull downward. Some pits can develop horizontally, and seldom in the upward direction (Fontana & Greene 1983). They also vary in shapes, and some of the commons are shown in Figure 6. Pitting is the result of a process called auto-catalytic process. This progress involves a reaction in which its products are used further by one of the reactants. In the pitting case, it accelerates the corrosion rate at the pit’s bottom by excessive generation of ion M+. (Fontana & Green 1983.)

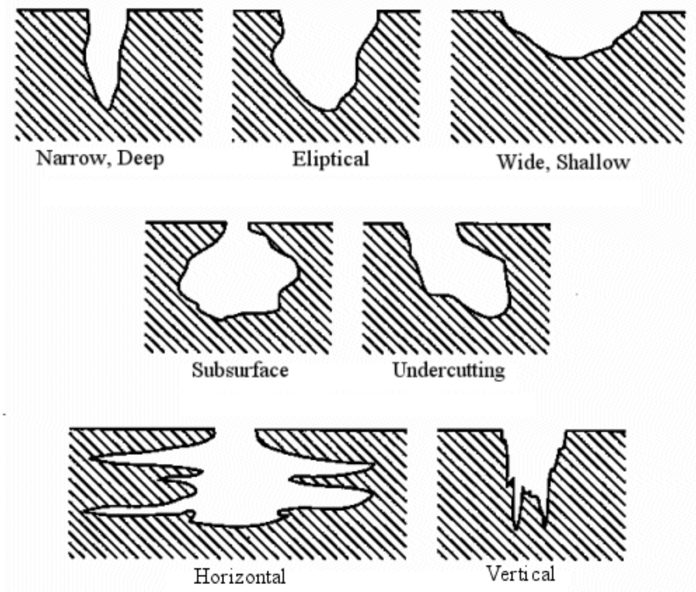


Figure 6: Pitting patterns (BYJU, 2019)

2.2.5 Inter-granular Corrosion

It is necessary to think about grain boundary when discussing this type of corrosion. A grain boundary, within a material, is the boundary between two crystallites of the material. For example, Figure 7 below shows the microscopic structure of low carbon steel (Fontana & Green 1983). It is possible to imagine that carbon steel is made of these black ”grains”, and the interface at which the grains touch each other is called grain boundaries. Now, in normal cases, the grain boundaries will have the same corrosion rate as the metal itself. But in some cases, these boundaries become more reactive than the grains itself. As a result, the boundaries are corroded rapidly. This could lead to the breaking between material grains and eventually cause them to fall apart. The phenomenon is called inter-granular corrosion. (Fontana & Green 1983.)

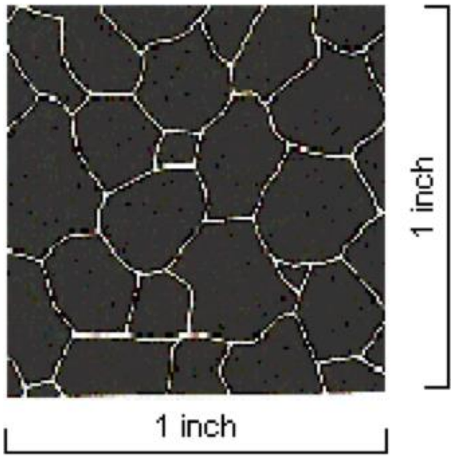


Figure 7: Structure of low carbon steel (Chegg, 2018)

There are several reasons behind this corrosion type. It could be that there are some impurities reside on the grain boundary. Additionally, the changes in amount of alloying elements within the metal could also cause inter-granular corrosion. For example, in stainless steel, if the amount of chromium starts to decrease, it could lead to corrosion in the grain boundaries. The presence of iron element in aluminium interface's region had shown the same effect. (Fontana & Greene 1983.)

2.2.6 Selective Leaching

Selective leaching or selective corrosion is corrosion which occurs within a metal alloy. In the progress, corrosion ”selects” and attacks one component of the alloy. For example, brass is composed of copper and zinc. Zinc has higher electrode potential (as discussed in 2.2.2 Galvanic Corrosion) and will suffer greater damaged by selective leaching. This phenomenon is referred as ”dezincification”. (Kopeliovich 2012). Because of its characteristics, selective leaching is also called ”de-alloying”. Some other alloys that are easily attacked by selective leaching include grey cast iron, aluminium alloys (de-aluminification), copper-nickels or several alloys that contain bronze. (Green & Maloney 1997.)

2.2.7 Erosion Corrosion

Erosion corrosion is the increasing of corrosion rate due to contact between the metal and a moving fluid. In pipelines, this type of corrosion is very likely to occur. In contrast to other types of corrosion like galvanic or selective leaching, in this case, the corrosion rate is accelerated by mechanical cause rather than chemical. Figure 8 presents some possible results of erosion corrosion. (Fontana & Green 1983.)

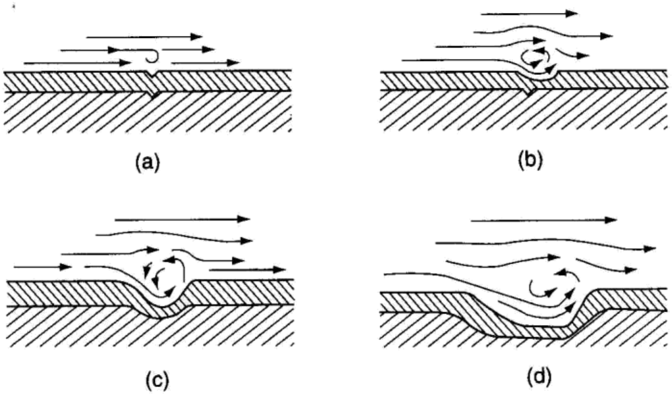
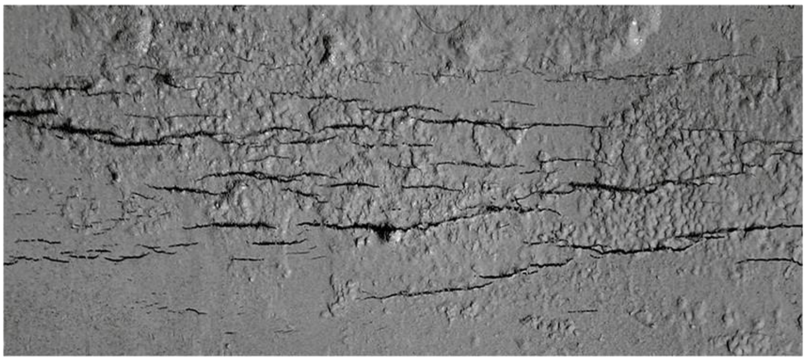


Figure 8: Erosion Corrosion Types (Corrosion Testing Lab 2010)

The flowing fluid cleans out protective layer(s) of corroding metal, leads to more exposing to the corrosive environment. Moreover, flow with high velocity and fluctuations (turbulent flows) can also cause pitting. Depending on the turbulent intensity, different shapes and sizes of pits will form on the corroding metal's surface, making the problem even more serious. (Fontana & Green 1983.)

2.2.8 Stress Corrosion

Stress corrosion is also called stress corrosion cracking (SCC), because it often results in cracks on the metal surface (see Picture 7). As the name suggests, SCC originates from the stress of material, or to be more exact, tensile stress. Different materials have different tensile strength, which means the ability to withstand the force that pulls them apart before they break. When metal pipes are placed in a corrosive environment and at the same time endured some types of tension (e.g underground), SCC can occur. (Degarmo, Black & Kohser 2003.)



Picture 7: Stress Corrosion (Zvirko, Olha & Savula 2016)

Sometimes, the cracks caused by SCC are hardly noticeable, even microscopic. Therefore, SCC can be a very dangerous and disastrous type of corrosion, since the early structure damage can only be detected under a microscope. As SCC gets more serious and leads to cracking, it can result in chemical leakage, pressure disturbance and possibly the destruction of a whole system. The Flixborough explosion case (1974) could be an example, when stress corrosion may have caused a crack in one reactor, starting a horrific reaction chain concluded in the disaster. There are some different types of SCC, namely chloride SCC or caustic SCC, depending on the chemical or mechanical factors that contribute to stress corrosion. (Roberge 2008.)

2.3 Corrosion in Piping System

Piping system (pipelines) is a transporting system consists of pipes, valves, pumps and other components. Pipelines are very essential to industrial plants, since they are used to transport materials and waste, keeping the system running smoothly. Sometimes, it only takes a small crack or leak in one pipe, resulted from corrosion, to create a disaster. Liquid transporting pipelines tend to suffer more, since they are subjected to wet corrosion, and erosion corrosion with flowing liquid. Pipes that are buried underground may endure tensile stress which lead to stress corrosion. (Roberge 1993.)

There are several case studies which can show the destructive nature of corrosion. For instance, Picture 8 was taken at the Mihama nuclear power plant, Japan after the incident in August, 2004. This pipe was transporting superheated steam (at 300^{o}C) and was blown open by the steam from inside. This is a result of, according to NISA (Japanese Nuclear and Industrial Safety Agency), corrosion and poor piping management. The pipe suffered from erosion corrosion, but it was not inspected and replaced in time. Wall thickness at the accident point had been reduced from 10mm to 1,5mm, therefore it could not endure internal pressure and led to the disaster. This accident resulted in severe steam leakage and five deaths. (Roberge 2007.) Another famous case is the Flixborough explosion, which was mentioned in stress corrosion section, although it was more about corroded reactor rather than pipelines. Since corrosion in piping system can cause serious failure to an industrial plant, it has to be monitored and controlled carefully. (Fotana & Green 1983.) Possible techniques to fight and protect the system from corrosion will be presented extensively in section 2.4 .

Picture 8: Transport pipe destroyed as a result of corrosion (Roberge 2007)

2.4 Corrosion Prevention & Solutions

In this section, methods to prevent and minimise corrosion will be discussed. Pipes can be made from cement, ceramic or plastic, but the most common are metallic pipes. For the thesis, only cases of metal corrosion are considered and therefore, it is necessary to focus on optimised solutions for metal pipes. The prevention methods ranging from the initial stage of buidling a pipeline system, including selection of piping material, or design system, towards the later stage when the system had already been built, such as altering the corroding environment or adding cathodic/anodic protection. (Fotana & Green 1983.) Advantages and disadvantages of each method is also discussed in this section.

2.4.1 Selection of Material

Before thinking of how to deal with corrosion, it is more beneficial to prevent them from happening in the first place. One of the most guaranteed methods is choosing the right material. It is necessary to consider the pipes' usage, the corrosive environments that they will be put in and will be put in them. This method requires careful planning and good material knowledge. (Fotana & Green 1983.)

When choosing material for pipelines, beside the metal's corrosion resistance, there are other factors that should be considered. Such factors could be the price of material, their availability, or the lifespan of the piping system. For example, titanium is very resistant to corrosion, but it is expensive and in some cases not necessary. It may be more beneficial to use stainless steel with protective coating. (Fontana & Greene 1983.) One method which could be used is the iso-corrosion matrix.

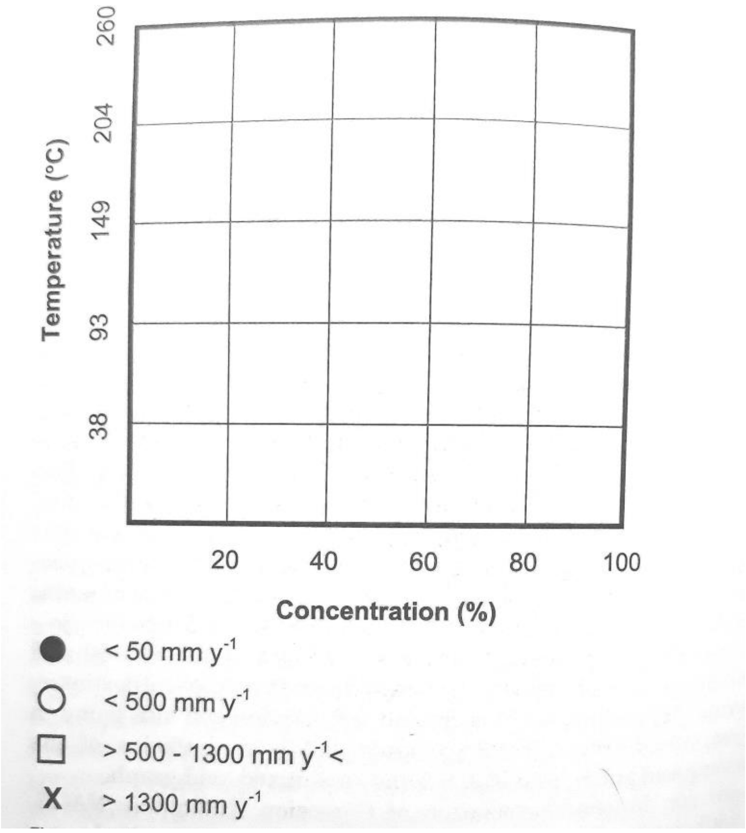


Figure 9: The iso-corrosion matrix (Roberge 2000)

Figure 9 shows the basic component of a simple iso-corrosion matrix. The matrix includes two axis which present concentration of the corrosive environment, and the temperature. There are different symbols that describe various corrosion rates that might occur. Figure 10 below presents an example use of this matrix. (Roberge 2000.)

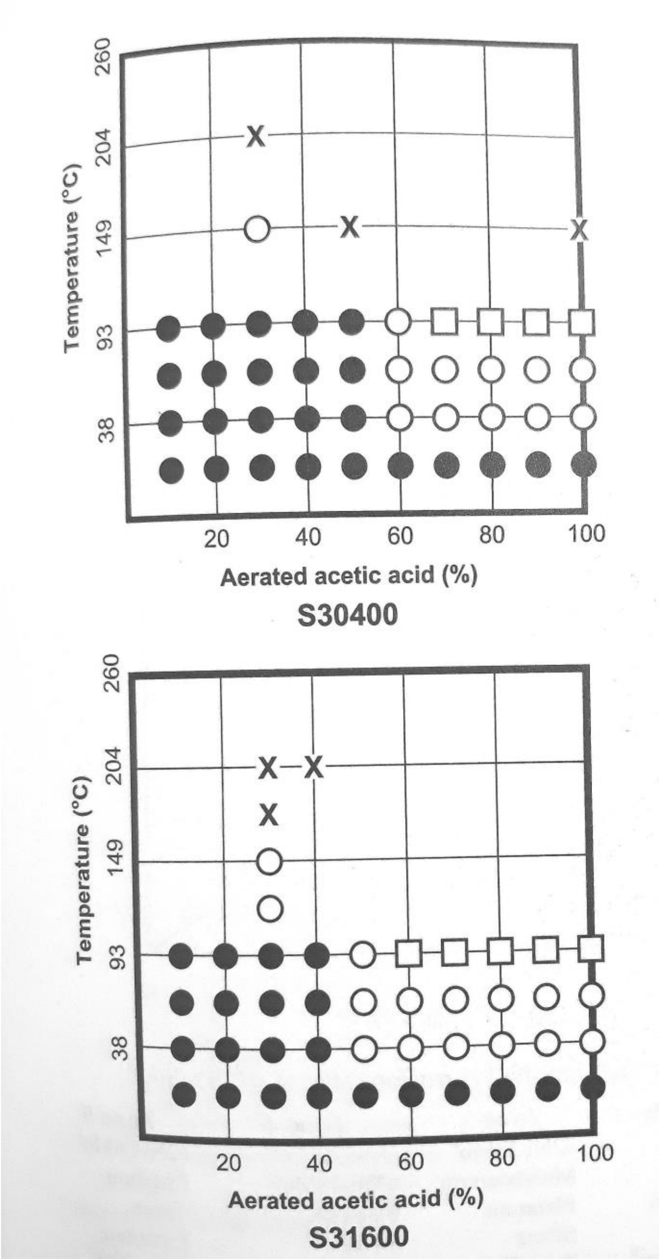


Figure 10: Corrosion diagram for S30400 and S31600 steel (Roberge 2000)

In a same corrosive environment, different materials result in different corrosion rates. The rate as well depends on the concentration and temperature of the environment, but choosing the right material is also important. Besides the iso-corrosion matrix, there are other corrosion rating systems for different metal that could be used to decide the suitable material. For instance, according to The Copper Development Association's database, copper (C11000) is very corrosion-resistant to calcium hydrochloride; but using tin brass (C42000) is not acceptable. (Roberge 2000.)

Mechanical properties of each material should also be considered. In some cases, if building structures that are prone to tensile stress, ordinary steel may be more resistant to stress corrosion and pitting than stainless steel. There is no material that can resist all types of corrosion, so choosing the right material for certain environments is vital in corrosion fighting. (Fontana & Greene 1983.)

2.4.2 Environment Modification

If the piping system has already been built, then material selection is not an option any more. Instead, it is possible to change environment they are located in. Factors like temperature, concentration of corrodents, or flow velocity greatly affects the corrosion rate. Therefore, altering them should help fighting corrosion. Generally, the decrease of temperature, corrosive substance’s concentration, or velocity will help slow down corrosion. Nonetheless, there are cases where changing temperature makes little or no effect on corrosion rate. Vacuum treatment of feed source can also be applied to remove oxygen containing in the input environment, hence preventing oxidation and corrosion. In working plants, these changes should be made only after careful inspections. (Fontana & Greene 1983.)

Corrosive environments can also be modified using corrosion inhibitors. Inhibitors are chemical compounds which can be sprayed or added in/onto the corrosive environments, whether they are gaseous or liquid, to decrease the corrosion rate. When they come in contact with metals or metal alloys, inhibitors form a protective layer on the material surface, protect them from further corrosion. Suitable inhibitors are chosen based on the characteristics of the material. For instance, benzotriazole ($C_6H_5N_3$) protects copper from corrosion and stains. (Finsgar & Milosev 2010.) Drying and moisture barrier substances can be as well used to reduce wet corrosion.

2.4.3 Cathodic and Anodic Protection

Cathodic and anodic protection means the interferences that turn all metal surface either into a cathode or anode. As it was discussed in 2.1.2 Corrosion Principles, in an electrochemical corrosion cell, the cathode receives positive current so it is protected from corrosion. Meanwhile, anodic protection helps form a passivated layer covering the metal surface, therefore slowing down corrosion. (Fontana & Greene 1983.) As a matter of fact, only metals which can form continuous passivated layer should be subjected to anodic protection (e.g see Figure 2).

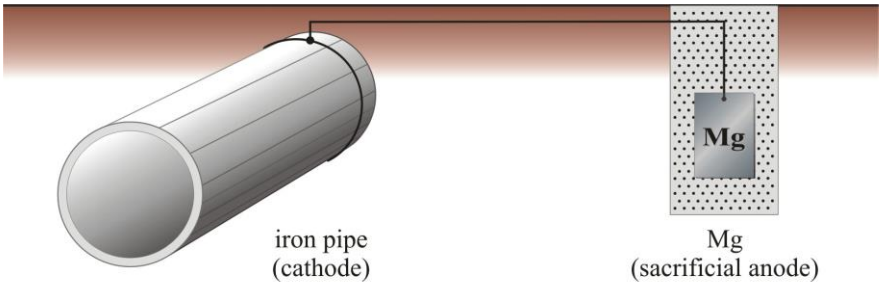


Figure 11: Sacrificial protection (Generalic 2020)

Figure 11 shows a common method of cathodic protection called ”sacrificial protection”. In this case, it is the iron pipe that needs to be protected, hence it has to be turned into a cathode. The iron pipe is therefore connected to a piece of magnesium, which acts as an anode and is corroded, shielding the iron pipe from corrosion. However, in extremely corrosive environment (e.g hot acid), the cost of cathodic protection and the contaminating risk is high. In those cases, anodic protection is preferred, as only one piece of cathode metal (usually noble) is necessary to control large anode area. (Bradford 1993.)

2.4.4 Coatings

Instead of waiting for passivated layer to form, corrosion can be prevented by initial coating. The mechanism of coating is rather simple: cover the metal surface with a protective layer. It is not different from painting houses, ”coating” the walls with paint to prevents moisture and dirt. Common coatings are paint, plastic, or other metals like zinc and aluminium. There could be more than one layer of coating to optimise protection. (EONCoat 2020.)

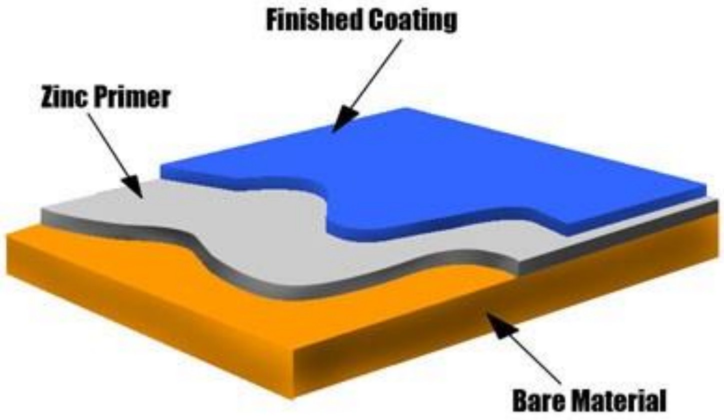


Figure 12: Two layer coating (LoD Offroad 2003)

Figure 12 presents a method of two-layer coating, which is used to shield cars from corrosion. The prime coating is zinc, which helps prevent corrosion, and a finished coating to protect the zinc layer. (LoD Offroad 2003.) Coating is an effective method, but it takes a lot of time and money to maintain. Usually, it is necessary to inspect and re-apply the coating after an amount of time. (EONCoat 2020.)

2.4.5 Design

When constructing a piping system, besides material selection, designing good structures is also important in fighting corrosion. The placement of each component in the system, shapes and sizes of tanks, slopes and wall thickness of pipelines can all contribute to or prevent corrosion. Figure 13 describes the importance of design in fighting corrosion. (Bradford 1993.)

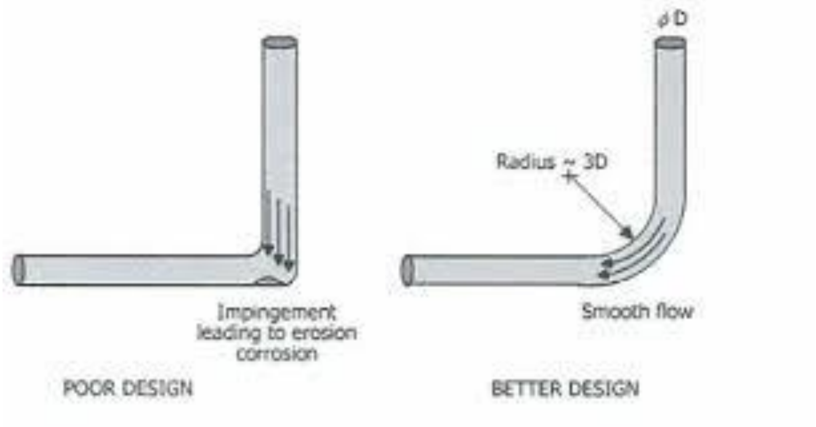


Figure 13: Affect of pipe design on corrosion (Osamah 2020)

In the left-sided pipe, the flow goes straight against the metal surface, attacks it with a force proportional to the flow's velocity and could result in erosion corrosion. Moreover, the levelled structure makes it difficult to empty the pipe totally, and would lead to resided substances inside the pipe. All of those problems can be resolved with a better design - as shown in the right-sided pipe (Osamah 2020). In general, it is best to avoid structures that could hold dirt, water, upward crevices or tanks that cannot be completely emptied (see Figure 14). Those design may collect unwanted contaminants and worsen the corrosion progress. (Bradford 1993.)

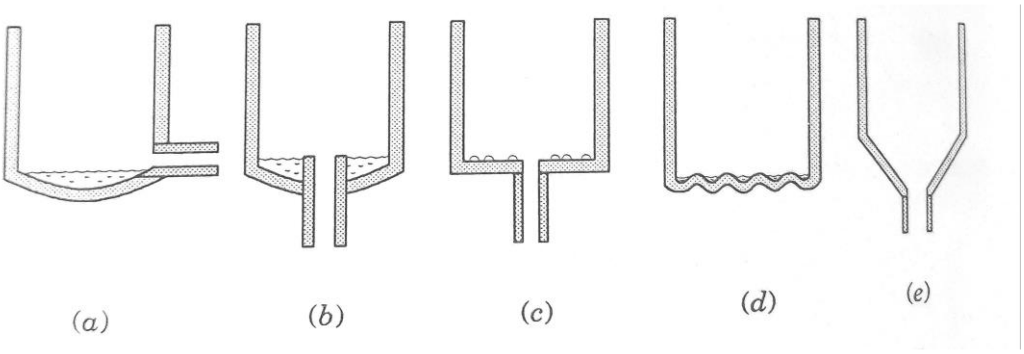


Figure 14: Examples of poor (a-d) and good (e) tank design (Bradford 1993)

3 PRACTICAL EXPERIMENT

In this section, several practical experiments were conducted. All the data collected from this experiment is recorded, calculated and subjected to discussion. The purpose of this practical work was to connect the theoretical part above to some possible situations related to corrosion in real life, and compare them to theory to see if they work accordingly. Research and experimental methodology which the experiments based on were also discussed in this part. The reliability and validity of the research were also mentioned.

3.1 Research Method

To retrieve data for a thesis, or a research in general, one could use either qualitative or quantitative method, each method works with a different type of data. Data collected by qualitative method is called qualitative data. These data are non-numerical and non-calculable. In other words, qualitative data could not be obtained by measuring parameters or using measuring tools; e.g languages, experiences, emotions and attitude. In qualitative research, data can be collected through surveys, forms, interviews, ethnography or studying previous data cases (case study). The result of qualitative data gives further understanding for social issues and examination. (McLeod 2019.).

Quantitative method, on the other hand, works with numerical data that can be recorded, measured and calculated, mostly through an experiment. Quantitative data can be used to support scientific study, and presented under the form of graphs, tables, and so on. Quantitative data can show a pattern and either prove or disprove a statement regarding the research’s topic. By analysing quantitative data, a natural phenomenon or a scientific issue could be explained and understood on a deeper level. (McLeod 2019.)

In this thesis, the quantitative research method was used for the practical work. Data were collected by conducting the experiment, and measuring numerical data from them (e.g mass, volume). The result of the experiment data can help achievie a deeper understanding of corrosion rate and the importance of material selection in preventing corrosion.

3.2 Experimental Method

As it has been discussed above, one of the most common methods to prevent corrosion is the selection of materials. Different metals in a same environment will have different corrosion rate, and it is the author’s responsibility to decide what metal is the most suitable for the experimented environment. This experiment is based on that theory, testing the importance of material selection in preventing pipeline corrosion. To conduct this experiment, it is neccesary to understand the concept of ”corrosion rate”. Corrosion rate describes the amount of material loss due to corrosion in a period of time. Usually, in processengineering, corrosion rate unit is $mm \cdot y^{-1}$. If this rate is written as r_c, it can be calculated by the equation below (Fontana & Greene 1983):

$$r_C = \frac{mm}{y} = \frac{wa - wi}{\rho \cdot A \cdot T} \tag{1}$$

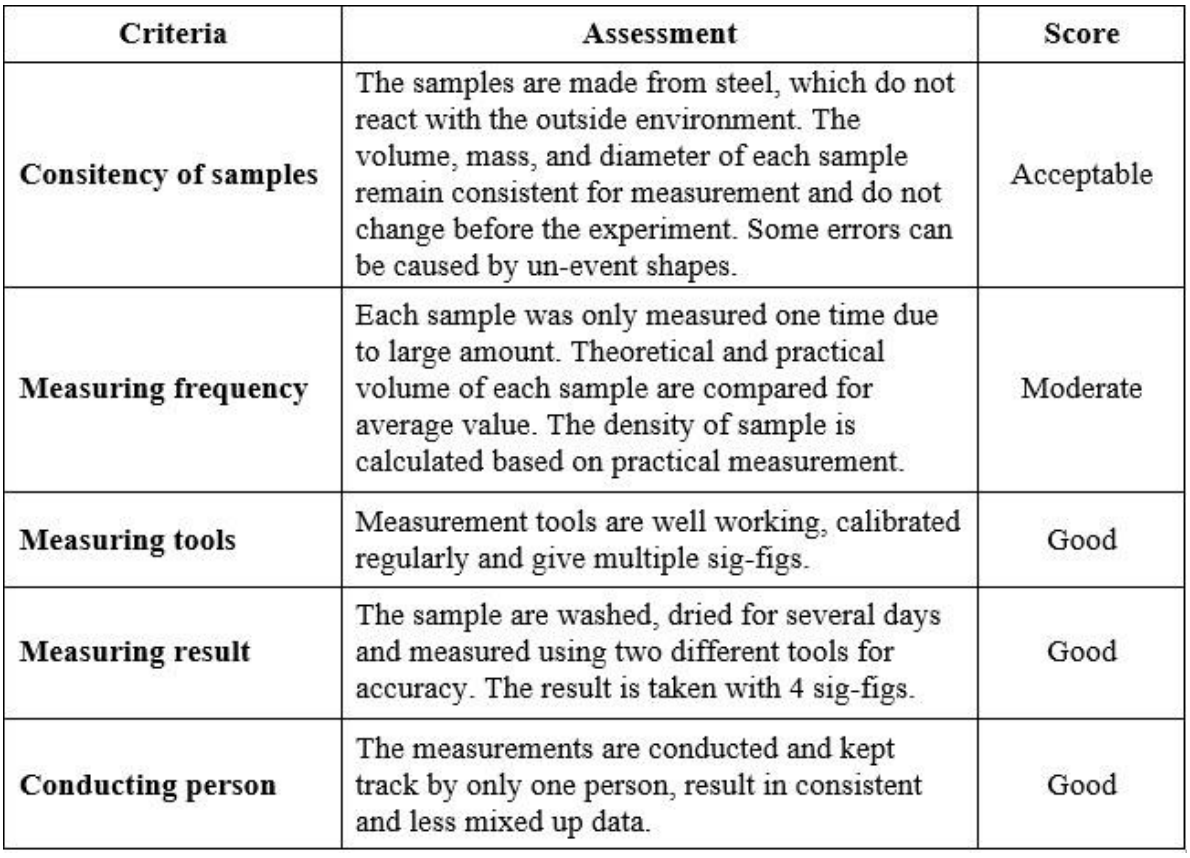
In which w_i is the initial weight of the metal (mg), w_a is the weight after T hours (corrosion time), A is the exposing area (cm^2) and ρ is the density of the metal (g/cm^3). Another unit for corrosion rate is mpy (mils penetration per year). This is mostly used in the USA and equals to 0,0254 $mm \cdot y^{-1}$
(Fontana & Greene 1983).

In this experiment, piping metal samples were labelled as S. These samples are used to make industrial pipe, so they are quite resistant to corrosion. The samples were put into different corrosive environment (all acidic) and left there for a certain amount of time. The initial weight, area and density of each sample were measured and calculated before placing them into the corrosive environment. After corrosion took place, the samples were measured again to determine the corrosion rate. They were also placed in contact to test galvanic corrosion.

3.3 Reliability and Validity

This thesis's experiments involve numerical data, which is measurable, so it is necessary to discuss the reliability and validity of the measurement techniques. The reliability regards the accuracy of the measurement, and whether the data measured is trustworthy for the research topic. The table below shows some criteria for this thesis' reliability and self-assessment score.

Table 2: List of criteria for research method



Criteria	Assessment	Score
Consitency of samples	The samples are made from steel, which do not react with the outside environment. The volume, mass, and diameter of each sample remain consistent for measurement and do not change before the experiment. Some errors can be caused by un-event shapes.	Acceptable
Measuring frequency	Each sample was only measured one time due to large amount. Theoretical and practical volume of each sample are compared for average value. The density of sample is calculated based on practical measurement.	Moderate
Measuring tools	Measurement tools are well working, calibrated regularly and give multiple sig-figs.	Good
Measuring result	The sample are washed, dried for several days and measured using two different tools for accuracy. The result is taken with 4 sig-figs.	Good
Conducting person	The measurements are conducted and kept track by only one person, result in consistent and less mixed up data.	Good

For the criteria listed above, it is safe to assume that the reliability of the measurement techniques is acceptable. The purpose of the research was to find out the corrosion rate of each sample in different environments. Hence, to ensure the validity of this research method, it is important that the mass before and after the corrosion time were measured correctly. To maintain the accuracy of mass measuring, an electric laboratory scale was used and calibrated regularly. The data recorded was taken into four sig-figs. The samples after corrosion were also washed and air-dried for several days before measuring to optimise validity.

3.4 Experimental Setup

This experiment consisted of two separate parts: normal corrosion and contact corrosion. For each part, same set of experimental subjects were used: three corrosive environment and three types of metal samples. The materials were labelled as M01, M02 and M03 for classification. Information about each sample, like compositions, name and quality was included in section Appendices.

Table 3: Chemicals and equipment required for the experiment

Materials	Quantity
Sulfuric acid H_2SO_4 1M	$\approx$ 150ml
Hydrochloric acid HCl 1M	$\approx$ 150ml
Nitric acid HNO_3 1M	$\approx$ 150ml
M01	18 pieces
M02	18 pieces
M03	18 pieces
Glass pipette	1
Suction ball	1
Beaker	-
Plastic pipet	-

Table 3 shows the equipment and chemicals used to conduct the experiment. The quantity of basic tools like beakers and plastic pipets is not necessary, so they were not listed in the table. In the normal corrosion case, the results of each experiment will be recorded according Table 4 below. For the contact corrosion experiment, the results will be recorded in the same manner. However, instead of ”S1” or ”S2”, it will be replaced with ”S1S2”, meaning a couple of metal placed in contact with each other. The purpose of that was to test the galvanic effect.

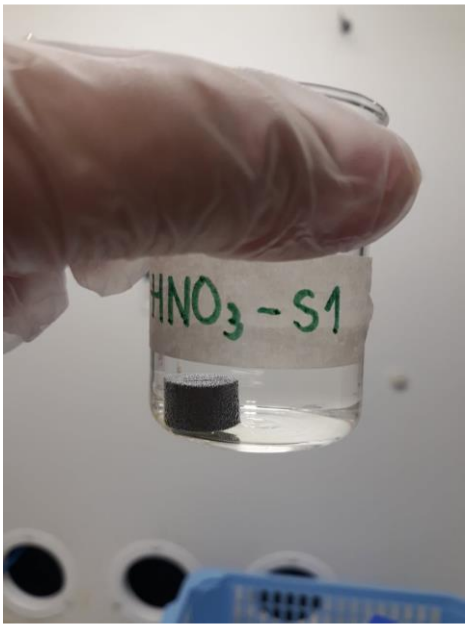
Table 4: Example resentation of results

	S1	**S2**	**S3**
Parameter 1	result	result	result
Parameter 2	result	result	result
Parameter 3	result	result	result

3.5 Experimental Procedure

The sample pieces were obtained and put in separate small beakers. Since all samples vary in shapes and sizes, the beakers holding them were labelled carefully. In the normal corrosion case, there were 9 beakers required in total. Each beaker contained 1 sample, and they were divided in three groups. Each group consisted of three beakers holding sample M01, M02 and M03.

For the contact corrosion test, there were also 9 beakers needed, each contained 2 samples. The samples were placed so that one beaker held 2 different samples. After that, all beaker are labelled with the corrosive environment, and the number of the samples which were put inside. For example, sample 1 in nitric acid was labelled HNO_3 - S1 as shown in Picture 9.



Picture 9: Sample labelling. Image taken at the laboratory.

When finished with labelling, the samples were taken to measurements. First of all, they are weighed with an electronic laboratory scale to determine the mass of each sample (up to 4 sig-figs). Consequently, the height and diameter of each sample were measured. As it can be observed from Picture 9, the samples used for experiment were in cylinder shape. Therefore, their theoretical volume and then their density can be calculated. However, the practical volume of each sample was also measured, by dropping them in a graduated cylinder filled with water, then record the displacement of water. All of these measurements are recorded and presented in section 4 Results.

Sulfuric, hydrochloric and nitric acid (all 1M) were obtained from the laboratory. They were poured into three beaker, approximately 150ml for each acid. A 20ml glass pipette was used to transfer the acid, together with a suction ball.

The sample containing beakers were placed firmly on flat surface. Using a glass pipette, 20ml of each acid was taken, and then put into each beakers with samples inside. After all the beakers had been filled with acid, they were covered with paraffin film and placed in a cool area with STP conditions. The corrosion progress started at 5pm on 14/01/2020 and finished at 12pm on 05/03/2020, lasting 1229 hours in total.

After that period of time, all the samples were taken out of their acid-filled beaker, then rinsed and brushed. They were follow-up weighed again to find out the mass loss during corrosion. It was necessary to treat the acidic sludge left in each beakers before disposing them. First of all, 10% NaOH solution was obtained and poured into a beaker. Using disposable plastic pipets, the basic solution was transferred into small beakers containing corrosive environment. They were then tested with pH paper until neutralised. The sludge inside those beakers was then put into vacuum filter to eliminate all the rusty solids. After that, the clean liquid could be poured down the drain. All the necessary data were recorded for calculations and discussion.

5 RESULTS & CALCULATIONS

In this section, results of the experiment are presented, as well as some calculations based on those results. Since the calculation progress is quite simple, for each value, there will be only one example equation. The other calculations were done by Excel and not included in the report.

5.1 Normal Corrosion

As it had been discussed above, this section involves results and calculations regrading the case of normal corrosion. Normal corrosion takes place when the samples are placed separately, each of them in one experimental beaker. There are no other samples or substances present with them in the corroding environment. The behaviours of samples in each environment (HNO_3, HCl and H_2SO_4 acid) are recorded and compared.

5.1.1 Normal Corrosion in HNO_3

The corrosion behaviour of each sample in HNO3 acid is presented in Table 5. The measured results are w_i (initial weight), w_a (weight after corrosion), d and h are diameter and height, and V_{meas} refers to the measured volume by water displacement. After that the average volume V_{av} can be calculated. The density ρ is calculated using theoretical equation.

Table 5: Results of normal corrosion in HNO_3

Samples & Parameters	**1**	**2**	**3**
w_i (g)	6,9141	7,0265	28,7667
w_a (g)	6,3263	7,0259	28,7637
d (mm)	11,95	11,95	30
h (mm)	7,8	7,75	5,2
V_{cal} (cm^3)	0,87	0,87	3,68
V_{meas} (cm3)	0,95	1	2,9
V_{av} (cm^3)	0,91	0,93	3,29
ρ (g/cm^3)	7,578	7,518	8,749

To start with the calculation, the theoretical volume of each sample was calculated. This volume is measured by the height and diameter of the sample. The theoretical volume Vcal is calculated by the following equation:

$$V = \pi . \frac{d^2}{4} . h \tag{2}$$

For example, the volume of sample 1 is calculated:

$$V = \pi . \frac{11{,}95^2}{4} . 7{,}80 = 874{,}82\text{mm}^3 = 0{,}87\text{cm}^3$$

The differences between theory and practical measurements could be the results of various factors. For example, the metal samples may not be perfect cylinders; or the instability of water temperature which can lead to density change. For more accuracy, the average of the measured and the theoretical volume will be taken, making V_{av} value which can be used to determine density. The density of one sample can be calculated by the following equation:

$$\rho = \frac{m}{V} \tag{3}$$

Take sample 1 as an instance, its density is determined as follow:

$$\rho_{s1} = \frac{m_{s1}}{V_{s1}} = \frac{6{,}9141}{0{,}91} = 7{,}578 \frac{g}{cm^3}$$

The same calculations were done to the other two samples. Now, the T value has already been recorded as 1229 hours. What is left to calculate is the area of each sample. Since the samples were fully submerged in the acid, surface area will be treated as contact area. The surface area of a cylinder is calculated as below:

$$A = 2\pi . \frac{d}{2} . h + 2\pi . \frac{d^2}{4} \tag{4}$$

An example calculation for sample 1 can be performed as below:

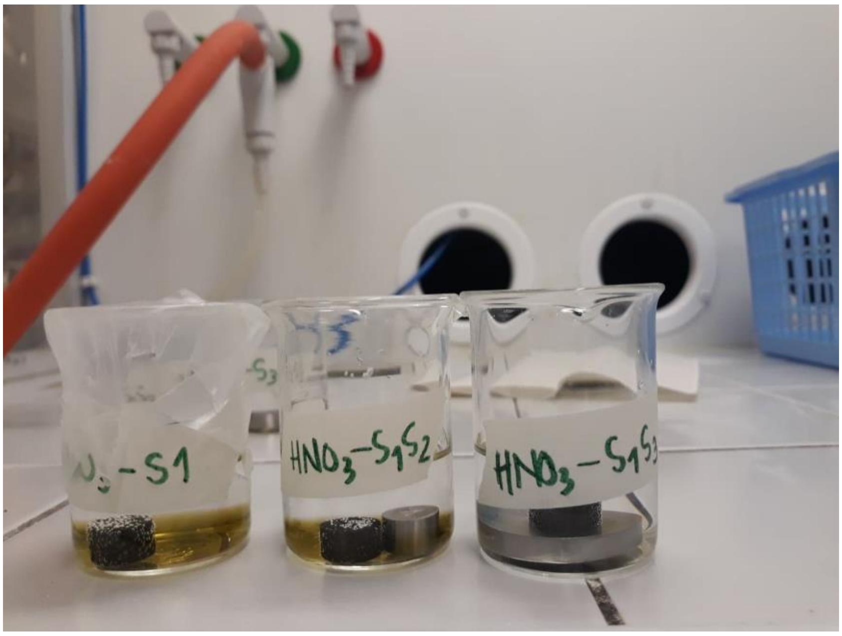
$$A_{s1} = 2\pi . \frac{11{,}95}{2} . 7{,}80 + 2\pi . \frac{11{,}95^2}{4} = 5{,}1714\text{mm}^2$$

As the area has been calculated, then all the parameters for finding the corrosion rate is ready. The corrosion rate rc will then be determined using Equation 1. The calculation results is presented in Table 6 below. As it can be seen in the table, sample 1 has the highest corrosion rate. In the HNO3 environment, sample 1 was also the first sample to react. Sample 2 has the lowest corrosion rate, which makes it the most resistance to acid nitric environment.

Table 6: Corrosion rate results for normal corrosion in HNO_3

Samples & Parameters	**1**	**2**	**3**
$A\ (mm^2)$	5,1714	5,1526	19,0381
$r_c\ (mm \cdot y^{-1})$	0,01069	$1{,}104 \cdot 10^{-5}$	$1{,}2837 \cdot 10^{-5}$

Picture 10 shows the sample in acid nitric solution. It was taken after adding the acid. It can be observed that sample 1 reacted almost immediately with the acid environment, forming a yellowish solution. Meanwhile, sample 2 and 3 showed little to no change. The reaction took place extremely quickly, as soon as the acid was added, sample 1 immediately showed signs of reaction. This could be a reasonable explaination for its significant weight loss compare to the other two samples.



Picture 10: Sample 1 react with HNO_3

5.1.2 Normal Corrosion in HCl

The corrosion behaviour of each sample in HCl acid is presented in the table below. The difference between the intinial weight and the weight after experimenting could suggest some ideas about how each sample react to corrosion, based on the weight loss. However to reach a more accurate conclusion, it is necessary to use the same calculation techniques which are presented above and determine the corrosion rate.

Table 7: Results of normal corrosion in HCl

Samples & Parameters	**1**	**2**	**3**
w_i (g)	8,9144	6,1803	30,6141
w_a (g)	8,4445	6,1192	30,4625
d (mm)	11,9	11,95	29,95
h (mm)	10	7,9	5,5
V_{cal} (cm^3)	1,1122	0,8860	3,8748
V_{meas} (cm^3)	1	0,95	2,5
V_{av} (cm^3)	1,0561	0,9180	3,18739
ρ (g/cm^3)	8,44086	6,7322	9,6048

Following the equations in the above section, the reaction area and corrosion rate for this case can be calculated. The results are listed in Table 8. If this result is compared to those in Table 6, it can be seen that the pattern is quite the same, with minor differences. Sample 1 has the highest corrosion rate, while 2 and 3 are slower. However, the corrosion rate of sample 1 had decreased, while 2 and 3 have higher corrosion rate. This suggests that hydrochlodirc acid is a more corrosive environment.

Table 8: Corrosion rate results for normal corrosion in HCl

Samples & Parameters	**1**	**2**	**3**
A (mm^2)	5,9629	5,2090	19,2651
r_c ($mm \cdot y^{-1}$)	0,0066545	0,0012419	0,0005840

5.1.3 Normal Corrosion in H_2SO_4

The corrosion behaviour of each sample in H_2SO_4 acid is presented in Table 9. The data are treated with the same calculating orders as previous samples in other acid environment. Though the measurements of samples are inevitably different, there are no abnormal behaviour recorded. The weight of each sample had decreased after the experiment, suggesting corrosion had occurred.

Table 9: Results of normal corrosion in H_2SO_4

Samples & Parameters	**1**	**2**	**3**
w_i (g)	7,0214	6,9717	28,2429
w_a (g)	5,7326	6,9703	28,2335
d (mm)	11,8	11,85	30
h (mm)	7,95	7,75	5,1
V_{cal} (cm^3)	0,8694	0,85473	3,605
V_{meas} (cm^3)	0,91	0,65	2,95
V_{av} (cm^3)	0,89	0,75	3,28
ρ (g/cm^3)	7,892	9,266	8,6172

The corrosion rate is calculated same as the previous cases and shown in Table 10. In this case, sample 1 still has the highest corrosion rate, and it is also the highest among the three environment. Sample 2 and 3 have insignificant rate and those are much lower in comparison with sample 1. So in general, if all samples are placed separately in corrosive environment, their corrosion rate in relation to each other is pretty much the same. However, there are some differences in how each sample reacts to a certain environment. For the record, the contact corrosion case is now analysed to see if there are any changes.

Table 10: Corrosion rate results for normal corrosion in H_2SO_4

Samples & Parameters	**1**	**2**	**3**
A (mm^2)	5,1343	5,0909	18,9438
r_c ($mm \cdot y^{-1}$)	0,022671312	$2{,}1153 \cdot 10^{-5}$	$4{,}10435 \cdot 10^{-5}$

5.2 Contact Corrosion

In this part of the experiment, the samples were placed in contact with each other, hence the name ”contact corrosion”. Th experiment is meant to see if this arrangement affects their corrosion rate, or has any major change on the way they react with the environment in general. For each environment, there are three contact couples: S1S2, S2S3 and S1S3. Each couple will be placed in a separated beaker and filled with the acid environment. The samples are arranged so that they have direct physical contact with each other to make the results more accurate.

5.2.1 Contact Corrosion in HNO_3

The contact corrosion behaviour of the samples in HNO_3 acid is presented in Table 11. The data were recorded in the same method as in the normal case, however, instead of just one sample, two samples were studied in this case. Measurements were recorded separately for each sample in a couple, so that the way they behave as one sample and in contact with another sample can be analysed as well. Basic calculations with volume, density and other propeties were done using Equation 2, 3 and 4. It should be noted that even thought they are labelled the same (for example “Sample 2”), each sample 2 in a couple has different measurements and therefore, they do not represent each other and are treated independently as an unique sample.

Table 11: Contact corrosion results for samples in HNO$_3$

Case and samples	**S1S2**		**S2S3**		**S1S3**	
	1	**2**	**2**	**3**	**1**	**3**
w_i (g)	6,0067	6,9692	7,136	30,7076	6,9384	29,0972
w_a (g)	5,0098	6,9681	7,1359	30,705	6,3469	29,0949
d (mm)	11,95	11,95	11,95	30	11,9	29,9
h (mm)	7,9	7,85	8	5,5	7,85	5,25
V_{cal} (cm^3)	0,8860	0,8804	0,8973	3,8877	0,8731	3,6863
V_{meas} (cm^3)	0,9	0,9	0,95	3,45	0,95	3,2
V_{av} (cm^3)	0,8930	0,8902	0,9236	3,6689	0,9115	3,4432
ρ (g/cm^3)	6,7263	7,8287	7,7261	8,3698	7,6117	8,4507

The calculations here are not different from what has been done in the normal corrosion case. Volumes can be determined by recorded height and width, and density ρ is found by dividing mass to volumes. Hence, the same steps are repeated, then the corrosion rates for each case could be easily calculated. The result is presented in Table 12 below. As it is presented in the table, sample 1 still has the highest corrosion rate, no matter if it reacts alone or within a couple.

Table 12: Corrosion rate results for contact corrosion in HNO$_3$

Case & Samples	**S1S2**		**S2S3**		**S1S3**	
	1	**2**	**2**	**3**	**1**	**3**
A (mm^2)	5,2090	5,1902	5,2465	19,3208	5,1591	18,9746
r_c	0,0203	$1{,}9296 \cdot 10^{-5}$	$1{,}75843 \cdot 10^{-6}$	$1{,}1460 \cdot 10^{-5}$	0,0107361	$1{,}0224 \cdot 10^{-5}$

5.2.2 Contact Corrosion in HCl

Table 13 shows the behaviour of samples in contact corrosion case, regarding HCl as a corrosive environment. The data is presented in the same manual as sulfuric acid cases. The order of the calculations is also the same, and therefore it is not necessary to include it again. The sampling couples are the same as in the acid sulfuric case.

Table 13: Contact corrosion results for samples in HCl

Case and samples	**S1S2**		**S2S3**		**S1S3**	
	1	**2**	**2**	**3**	**1**	**3**
w_i (g)	6,739	9,4185	9,5755	33,7428	8,5514	29,5412
w_a (g)	6,3023	9,4184	9,5631	33,5684	8,065	29,5103
d (mm)	11,9	11,9	11,9	29,95	11,95	29,9
h (mm)	7,65	10,5	10,7	6	9,75	5,5
V_{cal} (cm^3)	0,85083	1,16781	1,19006	4,22702	1,09353	3,86185
V_{meas} (cm^3)	0,9	0,9	0,95	3,45	0,95	3,2
V_{av} (cm^3)	0,87542	1,03391	1,07003	3,83851	1,02176	3,53092
ρ (g/cm^3)	7,69804	9,10963	8,94883	8,79059	8,36925	8,36642

Using Equation 2, 3, and 4, the necessary parameters can be calculated, such as density, volume and area. Consequently, the rates are determined by Equation 1. Table 14 shows the results for contact corrosion in hydrochloric acid. It can be observed that what happened here is quite the same as in normal corrosion, hydrochloric yields the highest corrosion rate for sample 2 and 3, while towards sample 1, the rate decreased. The reason for this phenomenon will be discussed in more detail in section 5 Interpretation and Discussion.

Table 14: Corrosion rate results for contact corrosion in HCl

Case & Samples	**S1S2**		**S2S3**		**S1S3**	
	1	**2**	**2**	**3**	**1**	**3**
A (mm^2)	5,08435	6,14982	6,22459	19,73552	5,90348	19,20943
r_c	0,00795	$1{,}272 \cdot 10^{-6}$	0,00016	0,00072	0,00702	0,00014

5.2.3 Contact Corrosion in H_2SO_4

Now, moving on to the last case of this experiment. The contact corrosion behaviour of the samples in H_2SO_4 acid is presented in Table 15. There are no unusual behaviour observed in the measuring data, they are quite stable and follow the same pattern as other contact corrosion cases. Therefore, they will be treated the same, using similar order of calculation and determination of values.

Table 15: Contact corrosion results for samples in H_2SO_4

Case and samples	**S1S2**		**S2S3**		**S1S3**	
	1	**2**	**2**	**3**	**1**	**3**
w_i (g)	8,5439	9,3628	7,0763	28,138	7,0118	27,8968
w_a (g)	7,2614	9,36	7,0743	28,1283	5,7422	27,8863
d (mm)	11,95	11,85	11,9	29,9	11,95	30
h (mm)	9,7	10,5	7,85	5,1	7,9	5,1
V_{cal} (cm^3)	1,0879	1,1580	0,8731	3,5810	0,8860	3,6050
V_{meas} (cm^3)	1	1,05	0,95	3,45	0,98	3,5
V_{av} (cm^3)	1,0440	1,1040	0,9115	3,5155	0,9330	3,5525
ρ (g/cm^3)	8,1841	8,4807	7,7630	8,0040	7,5152	7,8527

The calculation steps are just the same as with the previous cases. The corrosion rate results can be observed in Table 16. In this case, the outcome is rather similar to corrosion in nitric acid HNO_3. Sample 1 still has the highest corrosion rate, as its behaviour is stable through all the experiments. However, corrosion rate of sample 1 in this case is higher in comparsion with hydrochloric acid. The corrosion rate of sample 2 and 3, on another hand, is lower.

Table 16: Corrosion rate results for contact corrosion in H_2SO_4

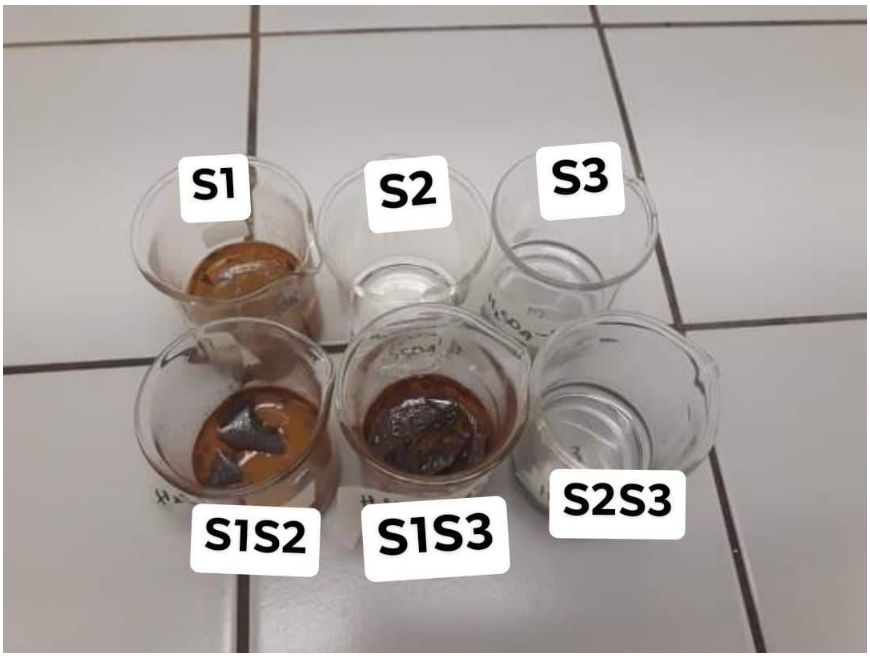
Case & Samples	**S1S2**		**S2S3**		**S1S3**	
	1	**2**	**2**	**3**	**1**	**3**
A (mm^2)	5,8847	6,1147	5,1591	18,8337	5,2090	18,9438
r_c	0,01898	$3{,}849 \cdot 10^{-5}$	$3{,}559 \cdot 10^{-5}$	$4{,}59 \cdot 10^{-5}$	0,02312	$5{,}031 \cdot 10^{-5}$

6 INTERPRETATTION & DISCUSSION

In this section, possible reasons behind all behaviour and results recorded from the experiment will be discussed. The certificate for each sample will be included in the Appendices section, and discussions will be based on them. So first of all, it is necessary to discuss the visual phenomenon after corrosion occured. Picture 11, 12 and 13 below show the phenomenon that happened after all the samples were left to corrode. As it can be seen in those pictures, all beakers with sample 1 had a brownish, rusty sludge inside, which is the result of corrosion. This phenomenon matches exactly with the numeral results: sample 1 always has the highest corrosion rate, and the first to react with all corrosive environment.

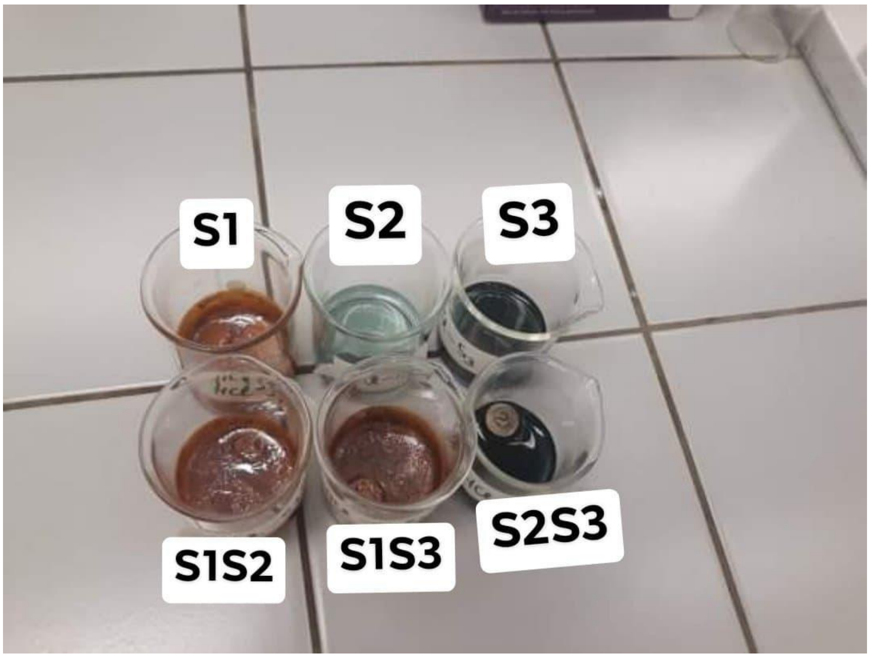
Picture 11: The corrosion of samples in HNO_3

Another aspect to notice is that, in hydrochloric acid case, some sample had reacted and created bluish green substances (see Picture 13). In this case, copper (II) chloride can be the first suggested substance, which has similar colour and might be the cause of this phenomenon. Nonetheless, the sample certificate (see Appendices) shows that only sample 1 has copper in its compositions, while beakers containing sample 2 and 3 also resulted in the mentioned colour. Moreover, copper (II) sulfate should result in the same blue colour, but in the reaction with sulfuric acid, it can be seen that the water is still transparent (see Picture 12).



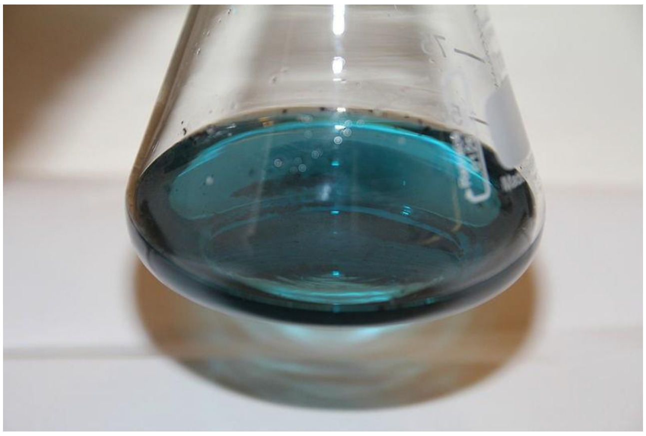
Picture 12: The corrosion of samples in H_2SO_4

To examine the sources of this phenomenon, the sample certificates should be involved. From the certificates, it is learnt that both sample 2 and 3 contain chromium (Cr). Upon reacting with hydrochloride acid, chromium can form either chromium (II) or (III) chloride ($CrCl_2$ or $CrCl_3$). This could be a reasonable explanation, since apart from chromium, there are no possible elements that can react with the ion Cl- and form the substance with the blue/green colour, which is seen in Picture 13.



Picture 13: The corrosion of samples in HCl

From Picture 14 below, the colour of the $CrCl_2$ solution can be observed. It is quite the same as the colour resulted from the experiment, while the $CrCl_3$ solution is more green. Therefore, it is reasonable to conclude that the colour of the solution is from chromium element reacts with ion chloride. Now, the corrosion rate is consequently analysed. To understand more about the characteristics of each samples, comparisons between normal corrosion and contact corrosion will be made. First, the data from nitric acid case in Table 6 and Table 12 should be considered. According to what the data present, when staying on their own, sample 1 has the fastest corrosion rate, while sample 2 and 3 corroded very slow and their mass were almost unchanged. However, upon looking at the contact corrosion rate table, some differences in each sample behaviour could be noticed. When placed in contact, for example, the S1S2 case, sample 1 corroded even faster. Its corrosion rate almost doubled, from 0,0106 to 0,0203 $mm \cdot y^{-1}$. The corrosion rate of sample 2 also increased, but not as much as sample 1. This could be a result of larger contact area, which led to more exposure. In the S2S3 case, the corrosion rate of sample 2 decreased significantly, while the corrosion rate of sample 3 stayed almost the same. In the S1S3 case, there was very little change in comparison to normal corrosion, but it can be observed that sample 1 corroded a bit faster and sample 3 corroded slower.



Picture 14: The colour of chromium (II) chloride solution (LHcheM 2012)

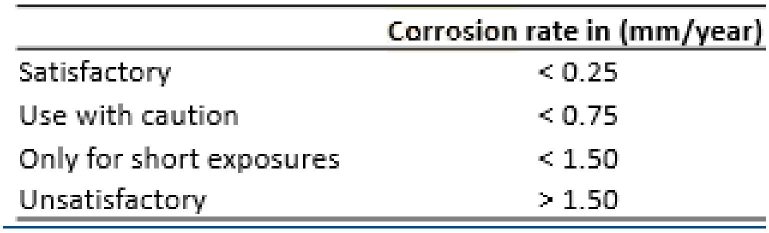
Now, corrosion in other two acid environments can be discussed. Data about them can be observed in Table 8 and Table 14 for hydrocholotic acid; along with Table 10 and 16. The pattern is rather the same with hydrochloric acid: sample 1 is always damaged faster, no matter what sample it is paired with. Sample 2 corroded slower and sample 3 corroded faster when placed in contact with each other. Nevertheless, in the sulfuric acid environment, there was no differences between two cases. The corrosion rate increased for each sample, but was not faster or slower their relation to each other.

So, to explain this phenomenon, it is necessary to take a look at their composition again (see Appendices). The reason why sample 1 always corrodes faster because, first of all, it contains less noble alloys. For example, aluminium Al has very low electrode potential E^0 (-1,662V), which makes it more prone to corrosion. In addition, sample 1 also has more carbon percentage, resulting in harder but more brittle steel. Sample 2 and 3 do not consist of aluminium, but instead; they have high percentage of chromium and molybdenum in their composition. These two had higher electrode potential (respectively -0,257V and -0.89V) and therefore they are more resistant to corrosion. (Harris 2007.)

Nonetheless, it is not just about the electrode potential. Chromium plays an essential role in making stainless steel ”stainless”. When exposed to corrosive environment, it reacts with oxygen, forming a passivated protection layer. This oxide layer cannot be observed by human eyes, since it is nano-scopic thin. When attacked by corrosion or other factors, the chromium layer can also heal itself: chromium in the steel keeps reacting until another layer is formed. Molybdenum, on the other hand, prevents the metal from pitting. (ISSF Staff 2020.) Since sample 2 and 3 have much larger percentage of these two elements, they are more resistant to corrosion than sample 1.

The mechanism is quite the same in the contact corrosion case. From the data in Table 1, it can be seen that sample 1 contains less chromium, hence it is lower on the galvanic series. Consequently, when placed against the other two, it becomes an anode and corrodes faster. Sample 3 has higher percentage of chromium, but lower nickel and higher percentage of carbon, which makes it less resistant to corrosion.

Table 17: Corrosion rate standards (Spruck 2008)



	Corrosion rate in (mm/year)
Satisfactory	< 0.25
Use with caution	< 0.75
Only for short exposures	< 1.50
Unsatisfactory	> 1.50

In Table 17, basic standards for corrosion rate in steel can be observed. They can be compared to Table 6, 8 and 10, which result in both sample 2 and 3 fall in the ”good” range, while sample 1 sometimes should be ”use with caution”. Sample 2 and 3 are resistant to all of the three acids when placed alone, they have low corrosion rate. However, in contact corrosion rate, sample 2 performs better and should be the main material. Hydrochloric acid results in high corrosion rate in all three samples when staying alone, but it can be minimised if they are paired (sacrificial metal). On the contrary, sulfuric acid is more corrosive to the samples when they are placed in contact with each other, so they work better alone. Sample 1 should be used with caution, and avoiding galvanic contact unless it is the sacrificial metal.

7 CONCLUSION

This thesis discusses metal corrosion, its mechanism and related prevention methods. Metal and metal alloys are common material for building pipelines system, which is an important transporting system in industrial plants. Corrosion of metal pipes can lead to serious issues, like cracking of pipes, chemical leakage, or in some cases even explosion. To control and prevent corrosion, it is necessary to understand its mechanism, in which ways it can happen and different types of corrosion. This thesis also mentioned some possible solutions and methods to fight corrosion, especially corrosion in the piping system.

One technique to minimise corrosion is material selection. By choosing the suitable metal for the environment surrounding and inside the piping system, corrosion can be prevented. This method, however, requires good knowledge in material characteristics. In the practical part of this thesis, testing on piping metal sample had been done, to see if they behave according to theory and compare their corrosion rate to the common standards. The experiment was also meant to prove the importance of correct metal selection.

From what has been discussed in chapter 5 Interpretation & Discussion, it is shown that all samples behave according to theory. Samples which are composed of less-resistance material corroded faster, in all corrosive environment; while samples which contained more resistant alloys resulted in less material loss. There were also changes in the corrosion rate of each sample in different environment, or when they are placed in contact. They also, in some cases, follow the galvanic behaviour, in which one metal becomes an anode and corroded faster. But in other cases, the samples did not show this pattern. Some samples can be used for one environment, but not the others.

In general, it is reasonable to conclude that choosing the right material is very essential in fighting corrosion. Because the same material can resist corrosion very well in one environment, but not the other ones. They can also behave differently depending on the metal they are paired with. Understanding the material’s characteristics can help building a sufficient piping system, which can resist corrosion, save resources and ensure safety. Corrosion is still a complex issue, which promotes continuous study and research, especially in the piping system. To process engineers, careful, thorough planning and design are necessary to fight against this phenomenon.

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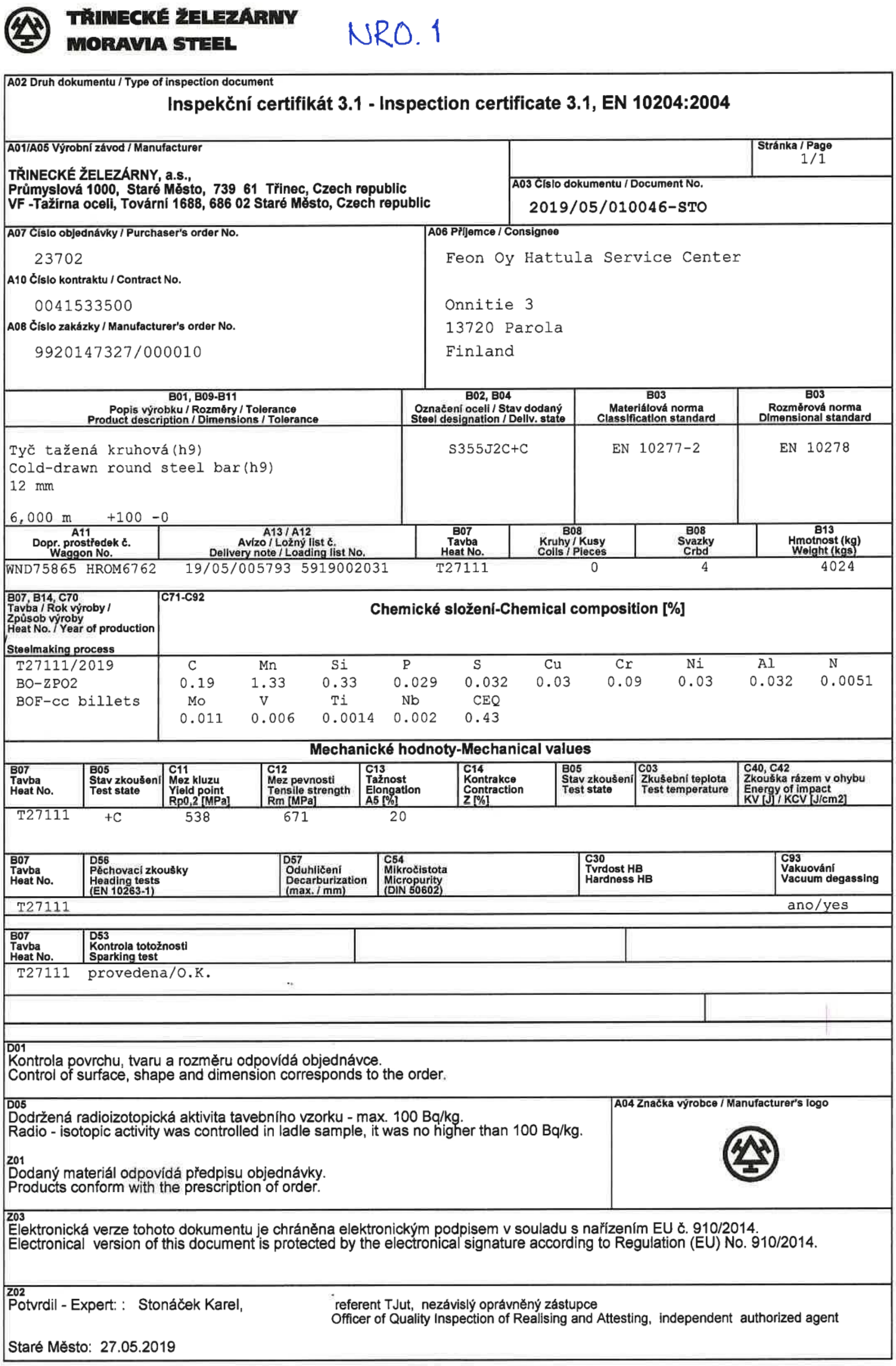
APPENDICES



TŘINECKÉ ŽELEZÁRNY
MORAVIA STEEL

NRO. 1

A02 Druh dokumentu / Type of inspection document

Inspekční certifikát 3.1 - Inspection certificate 3.1, EN 10204:2004

A01/A05 Výrobní závod / Manufacturer **TŘINECKÉ ŽELEZÁRNY, a.s.,** **Průmyslová 1000, Staré Město, 739 61 Třinec, Czech republic** **VF -Tažírna oceli, Tovární 1688, 686 02 Staré Město, Czech republic**	Stránka / Page 1/1 A03 Číslo dokumentu / Document No. 2019/05/010046-STO
A07 Číslo objednávky / Purchaser's order No. 23702 A10 Číslo kontraktu / Contract No. 0041533500 A08 Číslo zakázky / Manufacturer's order No. 9920147327/000010	A06 Příjemce / Consignee Feon Oy Hattula Service Center Onnitie 3 13720 Parola Finland

B01, B09-B11 Popis výrobku / Rozměry / Tolerance Product description / Dimensions / Tolerance	B02, B04 Označení oceli / Stav dodaný Steel designation / Deliv. state	B03 Materiálová norma Classification standard	B03 Rozměrová norma Dimensional standard
Tyč tažená kruhová (h9) Cold-drawn round steel bar (h9) 12 mm 6,000 m +100 -0	S355J2C+C	EN 10277-2	EN 10278

A11 Dopr. prostředek č. Waggon No.	A13 / A12 Avízo / Ložný list č. Delivery note / Loading list No.	B07 Tavba Heat No.	B08 Kruhy / Kusy Coils / Pieces	B08 Svazky Crbd	B13 Hmotnost (kg) Weight (kgs)
WND75865 HROM6762	19/05/005793 5919002031	T27111	0	4	4024

B07, B14, C70 Tavba / Rok výroby / Způsob výroby Heat No. / Year of production Steelmaking process	C71-C92 **Chemické složení-Chemical composition [%]**									
T27111/2019 BO-ZPO2 BOF-cc billets	C	Mn	Si	P	S	Cu	Cr	Ni	Al	N
	0.19	1.33	0.33	0.029	0.032	0.03	0.09	0.03	0.032	0.0051
	Mo	V	Ti	Nb	CEQ					
	0.011	0.006	0.0014	0.002	0.43					

Mechanické hodnoty-Mechanical values

B07 Tavba Heat No.	B05 Stav zkoušení Test state	C11 Mez kluzu Yield point Rp0,2 [MPa]	C12 Mez pevnosti Tensile strength Rm [MPa]	C13 Tažnost Elongation A5 [%]	C14 Kontrakce Contraction Z [%]	B05 Stav zkoušení Test state	C03 Zkušební teplota Test temperature	C40, C42 Zkouška rázem v ohybu Energy of impact KV [J] / KCV [J/cm2]
T27111	+C	538	671	20				

B07 Tavba Heat No.	D56 Pěchovací zkoušky Heading tests (EN 10263-1)	D57 Oduhličení Decarburization (max. / mm)	C54 Mikročistota Micropurity (DIN 50602)	C30 Tvrdost HB Hardness HB	C93 Vakuování Vacuum degassing
T27111					ano/yes

B07 Tavba Heat No.	D53 Kontrola totožnosti Sparking test		
T27111	provedena/O.K.		

D01
Kontrola povrchu, tvaru a rozměru odpovídá objednávce.
Control of surface, shape and dimension corresponds to the order.

D05
Dodržená radioizotopická aktivita tavebního vzorku - max. 100 Bq/kg.
Radio - isotopic activity was controlled in ladle sample, it was no higher than 100 Bq/kg.

Z01
Dodaný materiál odpovídá předpisu objednávky.
Products conform with the prescription of order.

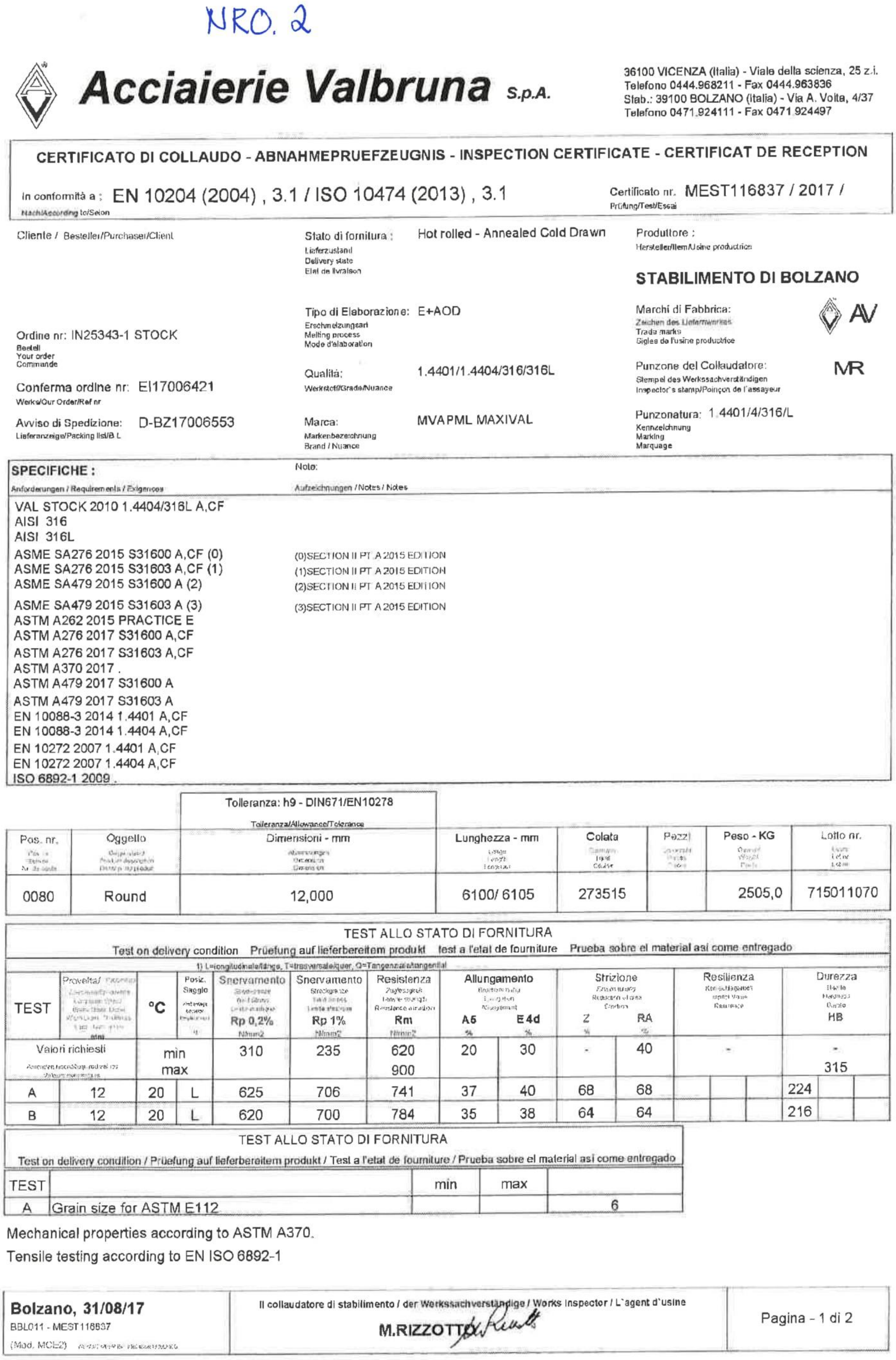
A04 Značka výrobce / Manufacturer's logo

Z03
Elektronická verze tohoto dokumentu je chráněna elektronickým podpisem v souladu s nařízením EU č. 910/2014.
Electronical version of this document is protected by the electronical signature according to Regulation (EU) No. 910/2014.

Z02
Potvrdil - Expert: : Stonáček Karel, referent TJut, nezávislý oprávněný zástupce
Officer of Quality Inspection of Realising and Attesting, independent authorized agent

Staré Město: 27.05.2019

APPENDIX 1



NRO. 2

Acciaierie Valbruna S.p.A.

36100 VICENZA (Italia) - Viale della scienza, 25 z.i.
Telefono 0444.968211 - Fax 0444.963836
Stab.: 39100 BOLZANO (Italia) - Via A. Volta, 4/37
Telefono 0471.924111 - Fax 0471.924497

CERTIFICATO DI COLLAUDO - ABNAHMEPRUEFZEUGNIS - INSPECTION CERTIFICATE - CERTIFICAT DE RECEPTION

In conformità a : EN 10204 (2004) , 3.1 / ISO 10474 (2013) , 3.1
Nach/According to/Selon

Certificato nr. MEST116837 / 2017 /
Prüfung/Test/Essai

Cliente / Besteller/Purchaser/Client

Ordine nr: IN25343-1 STOCK
Bestell
Your order
Commande

Conferma ordine nr: EI17006421
Werks/Our Order/Ref nr

Avviso di Spedizione: D-BZ17006553
Lieferanzeige/Packing list/B L

Stato di fornitura : Hot rolled - Annealed Cold Drawn
Lieferzustand
Delivery state
Etat de livraison

Tipo di Elaborazione: E+AOD
Erschmelzungsart
Melting process
Mode d'élaboration

Qualità: 1.4401/1.4404/316/316L
Werkstoff/Grade/Nuance

Marca: MVAPML MAXIVAL
Markenbezeichnung
Brand / Nuance

Produttore :
Hersteller/Item/Usine productrice

STABILIMENTO DI BOLZANO

Marchi di Fabbrica: AV
Zeichen des Lieferwerkes
Trade marks
Sigles de l'usine productrice

Punzone del Collaudatore: MR
Stempel des Werkssachverständigen
Inspector's stamp/Poinçon de l'assayeur

Punzonatura: 1.4401/4/316/L
Kennzeichnung
Marking
Marquage

SPECIFICHE :
Anforderungen / Requirements / Exigences

VAL STOCK 2010 1.4404/316L A,CF
AISI 316
AISI 316L
ASME SA276 2015 S31600 A,CF (0)
ASME SA276 2015 S31603 A,CF (1)
ASME SA479 2015 S31600 A (2)
ASME SA479 2015 S31603 A (3)
ASTM A262 2015 PRACTICE E
ASTM A276 2017 S31600 A,CF
ASTM A276 2017 S31603 A,CF
ASTM A370 2017 .
ASTM A479 2017 S31600 A
ASTM A479 2017 S31603 A
EN 10088-3 2014 1.4401 A,CF
EN 10088-3 2014 1.4404 A,CF
EN 10272 2007 1.4401 A,CF
EN 10272 2007 1.4404 A,CF
ISO 6892-1 2009 .

Note:
Aufzeichnungen / Notes / Notes

(0)SECTION II PT A 2015 EDITION
(1)SECTION II PT A 2015 EDITION
(2)SECTION II PT A 2015 EDITION
(3)SECTION II PT A 2015 EDITION

Tolleranza: h9 - DIN671/EN10278
Tolleranza/Allowance/Tolerance

Pos. nr.	Oggetto	Dimensioni - mm	Lunghezza - mm	Colata	Pezzi	Peso - KG	Lotto nr.
0080	Round	12,000	6100/ 6105	273515		2505,0	715011070

TEST ALLO STATO DI FORNITURA

Test on delivery condition Prüfung auf lieferbereitem produkt test a l'etat de fourniture Prueba sobre el material asi come entregado

1) L=longitudinale/länge, T=trasversale/quer, Q=Tangenziale/tangential

TEST	Provetta/	°C	Posiz. Saggio	Snervamento Rp 0,2% N/mm2	Snervamento Rp 1% N/mm2	Resistenza Rm N/mm2	Allungamento A5 %	E 4d %	Strizione Z %	RA %	Resilienza			Durezza HB		
Valori richiesti		min max		310	235	620 900	20	30	-	40	-			- 315		
A	12	20	L	625	706	741	37	40	68	68				224		
B	12	20	L	620	700	784	35	38	64	64				216		

TEST ALLO STATO DI FORNITURA

Test on delivery condition / Prüfung auf lieferbereitem produkt / Test a l'etat de fourniture / Prueba sobre el material asi come entregado

TEST		min	max	
A	Grain size for ASTM E112			6

Mechanical properties according to ASTM A370.
Tensile testing according to EN ISO 6892-1

Bolzano, 31/08/17
BBL011 - MEST116837
(Mod. MCE2)

Il collaudatore di stabilimento / der Werkssachverständige / Works inspector / L'agent d'usine
M.RIZZOTTO

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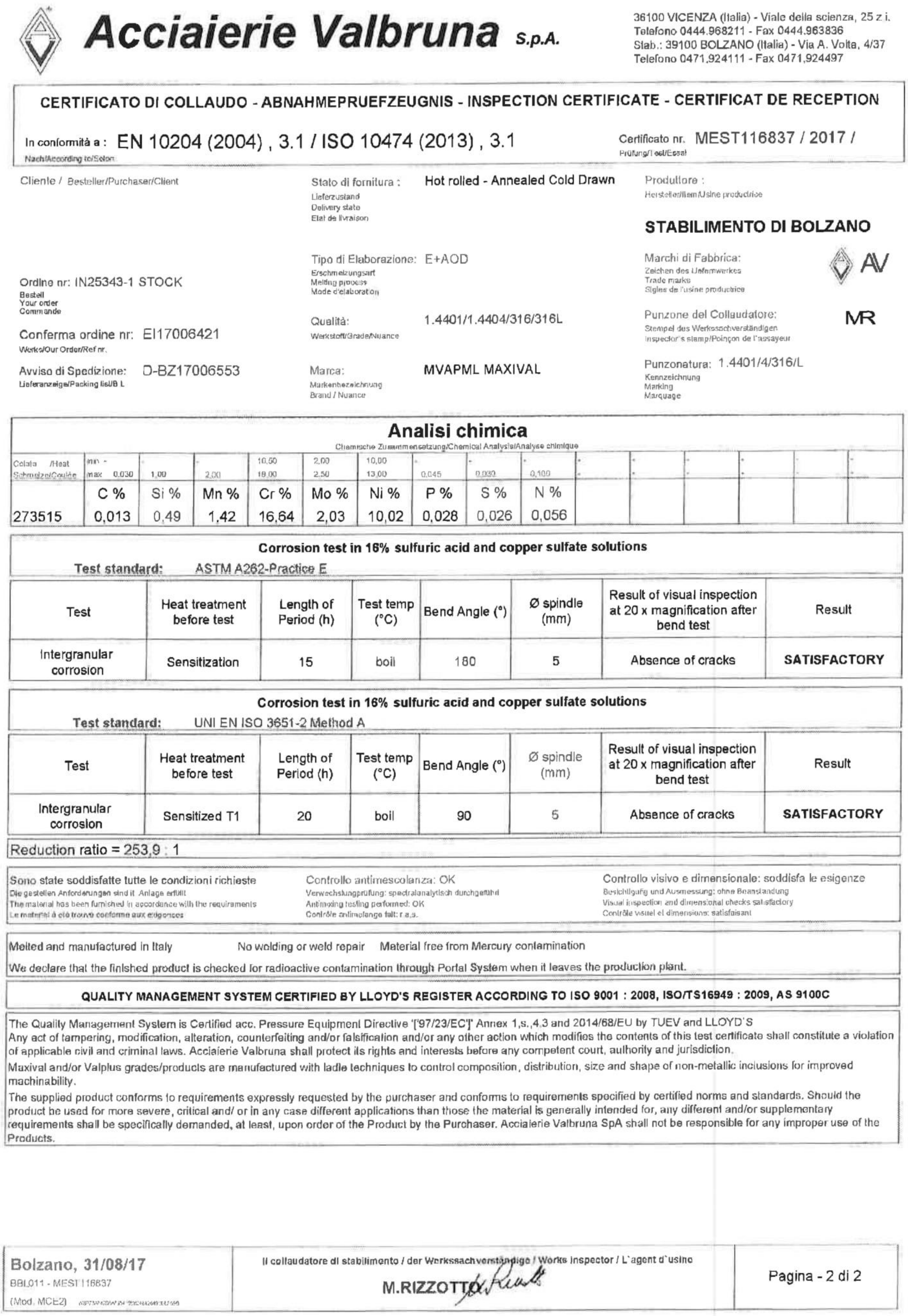

Acciaierie Valbruna S.p.A.

36100 VICENZA (Italia) - Viale della scienza, 25 z.i.
Telefono 0444.968211 - Fax 0444.963836
Stab.: 39100 BOLZANO (Italia) - Via A. Volta, 4/37
Telefono 0471.924111 - Fax 0471.924497

CERTIFICATO DI COLLAUDO - ABNAHMEPRUEFZEUGNIS - INSPECTION CERTIFICATE - CERTIFICAT DE RECEPTION

In conformità a : EN 10204 (2004) , 3.1 / ISO 10474 (2013) , 3.1
Nach/According to/Selon

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Kennzeichnung
Marking
Marquage

Analisi chimica

Chemische Zusammensetzung/Chemical Analysis/Analyse chimique

Colata /Heat Schmelze/Coulée	min - max 0,030	- 1,00	- 2,00	10,50 18,00	2,00 2,50	10,00 13,00	- 0,045	- 0,030	- 0,100	- -	- -	- -	- -	-	- -
	C %	Si %	Mn %	Cr %	Mo %	Ni %	P %	S %	N %						
273515	0,013	0,49	1,42	16,64	2,03	10,02	0,028	0,026	0,056						

Corrosion test in 16% sulfuric acid and copper sulfate solutions

Test standard: ASTM A262-Practice E

Test	Heat treatment before test	Length of Period (h)	Test temp (°C)	Bend Angle (°)	Ø spindle (mm)	Result of visual inspection at 20 x magnification after bend test	Result
Intergranular corrosion	Sensitization	15	boil	180	5	Absence of cracks	**SATISFACTORY**

Corrosion test in 16% sulfuric acid and copper sulfate solutions

Test standard: UNI EN ISO 3651-2 Method A

Test	Heat treatment before test	Length of Period (h)	Test temp (°C)	Bend Angle (°)	Ø spindle (mm)	Result of visual inspection at 20 x magnification after bend test	Result
Intergranular corrosion	Sensitized T1	20	boil	90	5	Absence of cracks	**SATISFACTORY**

Reduction ratio = 253,9 : 1

Sono state soddisfatte tutte le condizioni richieste
Die gestellen Anforderungen sind it. Anlage erfüllt
The material has been furnished in accordance with the requirements
Le matériel à été trouvé conforme aux exigences

Controllo antimescolanza: OK
Verwechslungprüfung: spectralanalytisch durchgeführt
Antimixing testing performed: OK
Contrôle antimelange fait: r.a.s.

Controllo visivo e dimensionale: soddisfa le esigenze
Besichtigung und Ausmessung: ohne Beanstandung
Visual inspection and dimensional checks satisfactory
Contrôle visuel et dimensions: satisfaisant

Melted and manufactured in Italy   No welding or weld repair   Material free from Mercury contamination

We declare that the finished product is checked for radioactive contamination through Portal System when it leaves the production plant.

QUALITY MANAGEMENT SYSTEM CERTIFIED BY LLOYD'S REGISTER ACCORDING TO ISO 9001 : 2008, ISO/TS16949 : 2009, AS 9100C

The Quality Management System is Certified acc. Pressure Equipment Directive '[97/23/EC]' Annex 1,s.,4.3 and 2014/68/EU by TUEV and LLOYD'S
Any act of tampering, modification, alteration, counterfeiting and/or falsification and/or any other action which modifies the contents of this test certificate shall constitute a violation of applicable civil and criminal laws. Acciaierie Valbruna shall protect its rights and interests before any competent court, authority and jurisdiction.

Maxival and/or Valplus grades/products are manufactured with ladle techniques to control composition, distribution, size and shape of non-metallic inclusions for improved machinability.

The supplied product conforms to requirements expressly requested by the purchaser and conforms to requirements specified by certified norms and standards. Should the product be used for more severe, critical and/ or in any case different applications than those the material is generally intended for, any different and/or supplementary requirements shall be specifically demanded, at least, upon order of the Product by the Purchaser. Acciaierie Valbruna SpA shall not be responsible for any improper use of the Products.

Bolzano, 31/08/17
BBL011 - MEST116837
(Mod. MCE2)

Il collaudatore di stabilimento / der Werkssachverständige / Works Inspector / L'agent d'usine
M.RIZZOTTO

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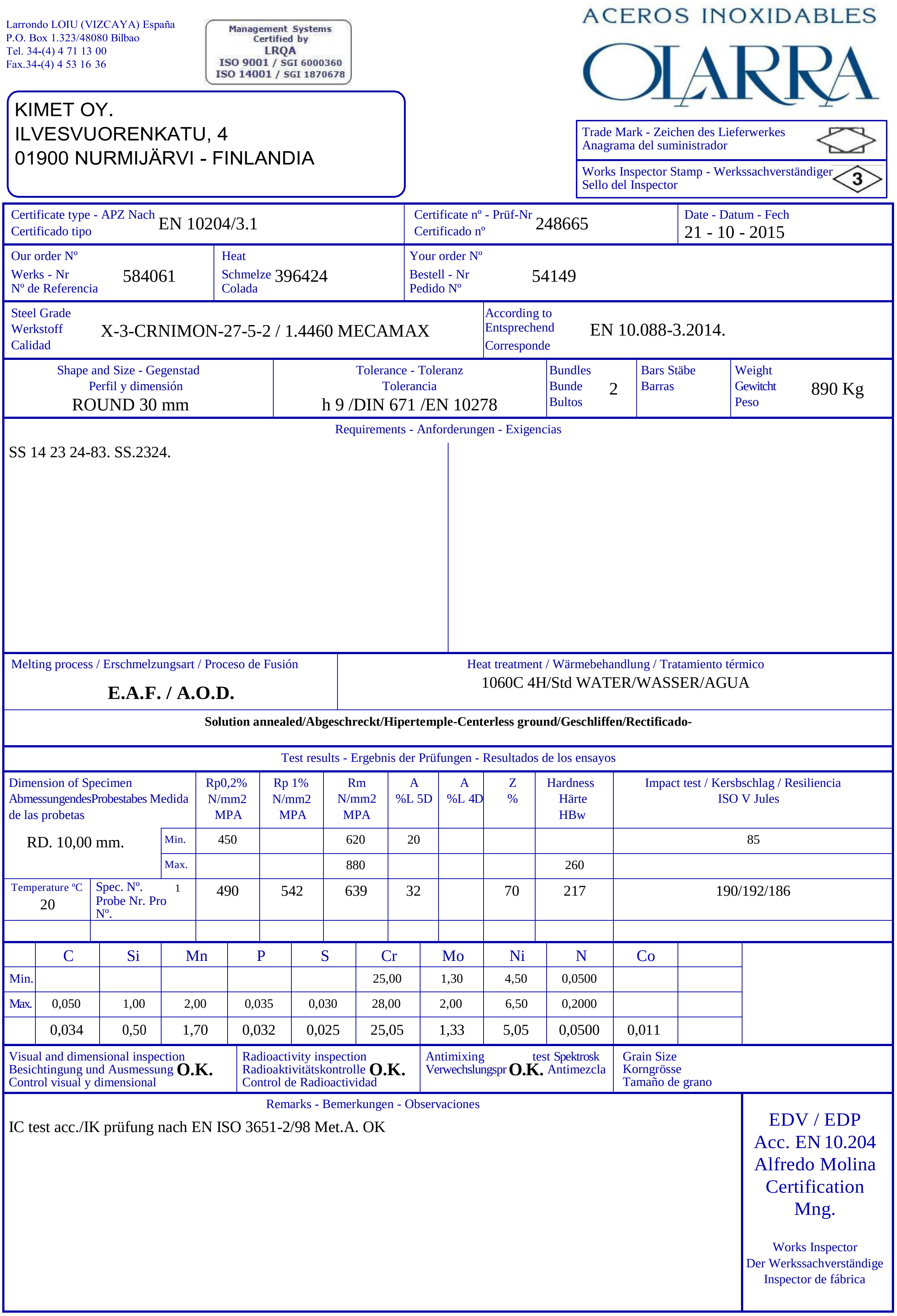
APPENDIX 2



Larrondo LOIU (VIZCAYA) España
P.O. Box 1.323/48080 Bilbao
Tel. 34-(4) 4 71 13 00
Fax.34-(4) 4 53 16 36

Management Systems
Certified by
LRQA
ISO 9001 / SGI 6000360
ISO 14001 / SGI 1870678

ACEROS INOXIDABLES
OLARRA

KIMET OY.
ILVESVUORENKATU, 4
01900 NURMIJÄRVI - FINLANDIA

Trade Mark - Zeichen des Lieferwerkes
Anagrama del suministrador

Works Inspector Stamp - Werkssachverständiger
Sello del Inspector
3

Certificate type - APZ Nach Certificado tipo	EN 10204/3.1	Certificate nº - Prüf-Nr Certificado nº	248665	Date - Datum - Fech	21 - 10 - 2015
Our order Nº Werks - Nr Nº de Referencia	584061	Heat Schmelze Colada	396424	Your order Nº Bestell - Nr Pedido Nº	54149
Steel Grade Werkstoff Calidad	X-3-CRNIMON-27-5-2 / 1.4460 MECAMAX	According to Entsprechend Corresponde	EN 10.088-3.2014.		

Shape and Size - Gegenstad Perfil y dimensión	Tolerance - Toleranz Tolerancia	Bundles Bunde Bultos	Bars Stäbe Barras	Weight Gewitcht Peso
ROUND 30 mm	h 9 /DIN 671 /EN 10278	2		890 Kg

Requirements - Anforderungen - Exigencias

SS 14 23 24-83. SS.2324.

Melting process / Erschmelzungsart / Proceso de Fusión	Heat treatment / Wärmebehandlung / Tratamiento térmico
E.A.F. / A.O.D.	1060C 4H/Std WATER/WASSER/AGUA

Solution annealed/Abgeschreckt/Hipertemple-Centerless ground/Geschliffen/Rectificado-

Test results - Ergebnis der Prüfungen - Resultados de los ensayos

Dimension of Specimen AbmessungendesProbestabes Medida de las probetas		Rp0,2% N/mm2 MPA	Rp 1% N/mm2 MPA	Rm N/mm2 MPA	A %L 5D	A %L 4D	Z %	Hardness Härte HBw	Impact test / Kersbschlag / Resiliencia ISO V Jules
RD. 10,00 mm.	Min.	450		620	20				85
	Max.			880				260	
Temperature ºC 20	Spec. Nº. 1 Probe Nr. Pro Nº.	490	542	639	32		70	217	190/192/186

	C	Si	Mn	P	S	Cr	Mo	Ni	N	Co	
Min.						25,00	1,30	4,50	0,0500		
Max.	0,050	1,00	2,00	0,035	0,030	28,00	2,00	6,50	0,2000		
	0,034	0,50	1,70	0,032	0,025	25,05	1,33	5,05	0,0500	0,011	

Visual and dimensional inspection Besichtingung und Ausmessung **O.K.** Control visual y dimensional	Radioactivity inspection Radioaktivitätskontrolle **O.K.** Control de Radioactividad	Antimixing test Spektrosk Verwechslungspr **O.K.** Antimezcla	Grain Size Korngrösse Tamaño de grano

Remarks - Bemerkungen - Observaciones

IC test acc./IK prüfung nach EN ISO 3651-2/98 Met.A. OK

EDV / EDP
Acc. EN 10.204
Alfredo Molina
Certification
Mng.

Works Inspector
Der Werkssachverständige
Inspector de fábrica

APPENDIX 3