

# A conceptual model describing Microbially Influenced Corrosion of sheet piles

**Additional Graduation Work**

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## Additional Graduation Work

by

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# Preface

This report is the final product of my Additional Graduation work. I chose the Additional Graduation Work for two reasons. First, I wanted to prepare myself for my thesis project. During this research I learned quite a lot of things that I would bring with me during my thesis project. I also wanted to know more about the relation between geotechnical engineering and chemistry. That is why I chose to research the influence of microorganisms on the corrosion of sheet piles

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Delft, May 2017*



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# Introduction

This report contains the description of the research performed to better understand corrosion of sheet piles. Sheet piles are long steel plates that are used in construction engineering. They are mainly, but not only, made of iron. Some other components that could be part of the steel are for example carbon, manganese, aluminium and chromium. Sheet piles have two main functions. The first one is that they can be used as a retaining structure ensuring the stability of a building pit. The second function is preventing fluids to move from one side to another. To guarantee the safety of a construction site, sheet pile walls should be reliable structures.

Corrosion of the sheet piles can reduce their reliability. Due to the corrosion of steel, the strength and impermeability of the walls decrease. Previous research, performed by Phd student Michael, investigated the influence of specific chemical species on the corrosion of steel. The research found out that in the case of sulphate present in the soil, the process of corrosion speeded up. In another case, where methane was found in the soil, a coating of iron carbonate formed on the surface of the sheet pile, preventing corrosion. In order to better understand these two corrosion processes, further research is needed. Therefore this research was set up.

The goal of this research is to describe the chemical reactions that occur in the soil that is in contact with iron. This is done by a literature study. Results and discoveries from previous researchers are analysed and compared. This study focussed on two things as said before: corrosion in sulphate rich environments and corrosion inhibition by a protective layer. This research gives therefore not a complete overview of corrosion processes, but is focused on two specific corrosion problems.

In order to be able to understand the two processes an introduction is given on corrosion. Chapter 2 first explains the way corrosion occurs and then focusses on microbially influenced corrosion. It was found that the main microorganisms that cause corrosion in the presence of sulphate are sulphate reducing bacteria. In Chapter 3 the role of these microorganisms is described. How a protective layer is formed is described in Chapter 4. In Chapter 5 the role of microorganisms is linked to a soil profile. This results in a detailed analysis of specific areas in the soil where the corrosion processes could take place. Chapter 6 concludes this report with a conceptual model, in which the corrosion processes are linked to the soil profile.



# 2

## Introduction to corrosion

Before describing the processes influencing corrosion a good understanding of corrosion is necessary. This chapter gives an introduction in the general corrosion process and corrosion influenced by microorganisms. Corrosion is defined as the loss of metal by reaction with the environment. Corrosion is both an electrochemical and a biochemical process (McCafferty, 2010). A pure electrochemical process is caused by the movement of electrical current. A biochemical process is a kind of electrochemical process, where the movement of energy occurs through metabolism. It occurs through the operation of coupled half-cell reactions also called redox reactions.

### 2.1. Corrosion process

In order for corrosion to occur an electrolytic or galvanic cell needs to be established. In an electrolytic cell the power needs to be supplied externally, while for a galvanic cell the reactions occur spontaneous (Gregory and Holmes, 2011). In soils no power is applied externally. Therefore in soils galvanic cells are established. Galvanic cells are formed when different areas of the surface develop different electrochemical potentials (Hamilton, 1985). Reasons for different electrochemical potentials could be inclusions in the metal, surface imperfections or the presence of a concentration cell. Figure 2.1 shows an example of an electrolytic and a galvanic cells. The cells consists of two sides: the anodic and the cathodic side. Electrons are exchanged from the anode to the cathode. In case of corrosion, the anode of the galvanic cell in Figure 2.1 would be iron. The electrolyte which is the contact between the anodic and the cathodic sides would be the water in the soil.

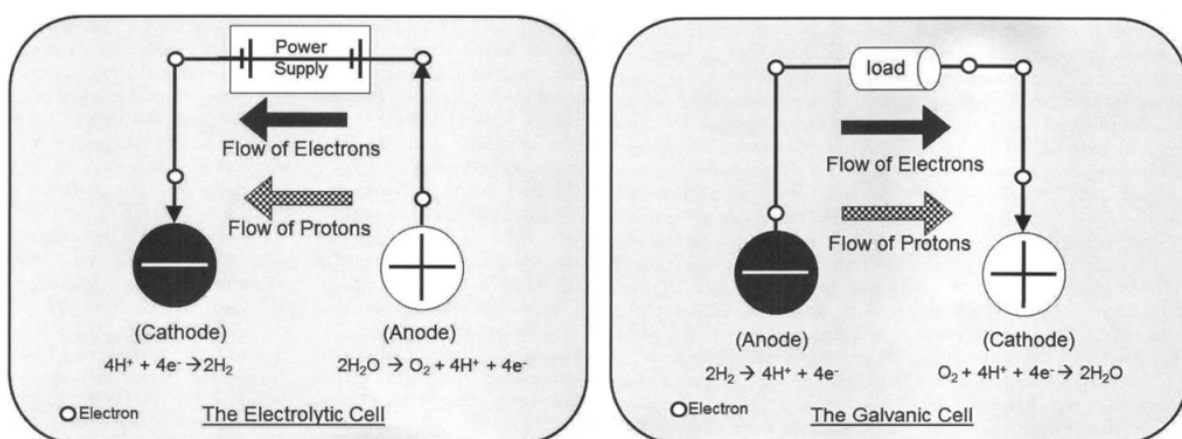


Figure 2.1: Difference between a Galvanic and an Electrolytic cell (Gregory and Holmes, 2011)

In the corrosion process iron acts as the electron donor. The anodic reaction of iron oxidation is given as:



There are different possible cathodic reactions that could contribute to the corrosion process. In aerobic environments oxygen is the electron acceptor. Figure 2.2 shows a sheet pile wall in the soil. In this case the anode is drawn deep in the soil. But oxidation of iron can take place at any location on the sheet pile. The cathode, where oxygen is reduced is drawn at the top. However there is always a small part of oxygen dissolved in water. So also the reduction of oxygen can take place at any location in the soil. Here it is drawn at the top, because the oxygen supply there is much larger than in the soil. The electrons are transferred from the anode to the cathode. The reduction reaction of oxygen is given in Reaction 2.2. Combining Reaction 2.2 with the oxidation reaction of iron, shown in Reaction 2.1, gives the overall reaction shown in Reaction 2.3. The oxidized iron and 2 hydroxide ions precipitate as  $\text{Fe(OH)}_2$ , given in Reaction 2.4

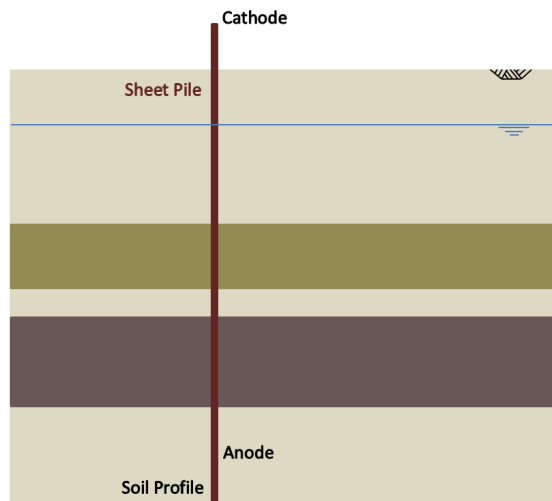
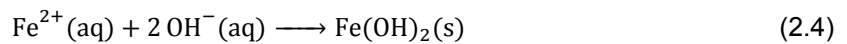
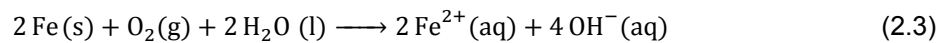


Figure 2.2: Soil profile with sheet pile wall

In anaerobic environments other chemical species act as electron acceptor. The cathodic reaction depends on the microorganisms present in the environment (Zarasvand and Rai, 2014). The coming section describes which and how microbes influence corrosion. Because the underground environment is in most cases anaerobic, this research will focus on corrosion processes in anaerobic environments. The cathodic reactions influencing anaerobic corrosion will be discussed in the coming chapters.

## 2.2. Microbially Influenced Corrosion

Microbial influenced corrosion (MIC) refers to the corrosion of surfaces influenced by the physiological processes of microorganisms (Vaughn-Thomas, n.d.). Microorganisms colonize in a biofilm, which is a gel containing 95% or even more water. The other 5% is a matrix of extracellular polymeric substances (EPS) in which the microbial cells grow (Videla and Herrera, 2005). Due to the production of EPS, biofilms are able to adhere to metal structures (Grooters et al., 2007).

In order for microorganisms to survive and grow in the soil they need to have access to water, an energy source, a carbon source, an electron donor and an electron acceptor (Vaughn-Thomas, n.d.). Microorganisms need water to be able to multiply. This is defined by the water activity ( $a_w$ -value). Water activity is defined as the ratio of vapour pressure of water in the soil to the vapour pressure of pure water at the same temperature (Schultz, 2016). It differs from water content in such way that water activity only accounts for 'available' water. If the water activity is below 0.9, microorganisms are not able to multiply and will therefore have no influence in the corrosion process (Beech et al., 2000). The energy source needed for MIC can come from all reduced chemical species (Beech et al., 2000). There are many possibilities to fulfil the energy and carbon source, depending on the specific microorganisms and the species present in the soil. In the coming chapters the specific energy and carbon sources will be given. In the case of iron corrosion the electron donor is of course iron. The electron acceptor is determined by the catabolic reaction which will be elaborated on in the coming chapters.

Biofilms can cause corrosion by inducing heterogeneities at the metal surface leading to a concentration cell (Videla and Herrera, 2005; Zarasvand and Rai, 2014). There are three types of concentration cells: metal ion-, oxygen- and passive-active concentration cells.

A metal ion concentration cell occurs in the presence of EPS. Below the EPS there are areas with high and low affinities for the metal surface (Zarasvand and Rai, 2014). At the location with high affinities for the metal surface iron oxidates faster, resulting in a higher concentration of  $\text{Fe}^{2+}$  ions. Metals in the presence of their own ions become cathodic (Javaherdashti, 2013). Therefore parts with high affinities become cathodic and parts with low affinities become anodic. Figure 2.3a shows schematically a sheet pile ( $\text{Fe}^0$ ) wall located in a soil. Different compounds are present in the soil, for instance water. A biofilm is attached to the metal surface leading to a metal ion concentration cell.

The second concentration cell is the oxygen concentration cell, as shown in Figure 2.3b. An oxygen concentration cell occurs where oxygen is not allowed to diffuse uniformly, so below a biofilm. Due to the heterogeneity of the distribution of biofilms multiple oxygen concentration cells occur (Zarasvand and Rai, 2014). The area of low-oxygen acts as the anode leading to corrosion in this area (Corrosion Technology Laboratory, n.d.).

The third concentration cell is the passive active cell. Passive active cells form when a biofilm layer on a metal surface breaks (Figure 2.3c). The metal below the break becomes active and will be open to corrosion. The passive film acts as a cathode, while the active metal acts as an anode (Zarasvand and Rai, 2014).

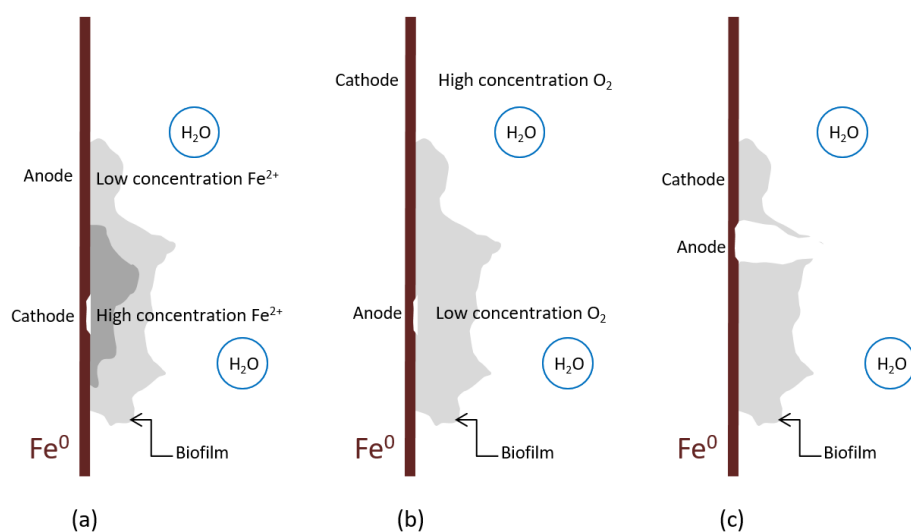


Figure 2.3: (a) A metal ion concentration cell (b) An oxygen concentration cell (c) An active passive cell

When a concentration cell is formed it is possible for corrosion to occur. However microorganisms present in the soil or in the biofilm are able to change different factors in the surrounding, accelerating or slowing down the electrochemical processes (Peng and Park, 1994).

### 2.2.1. Increasing corrosion rates

A lot of research has been done on the influences of microorganisms on corrosion rate. Lewandowski and Beyenal (2008) describe that microorganisms in a biofilm can stimulate the anodic and cathodic reactions by changing the redox conditions at the surface of the metal. Acidic metabolites are able to stimulate the anodic reaction (Videla and Herrera, 2005). The cathodic reaction could be stimulated by microbial production of a cathodic reactant (Videla and Herrera, 2005). Lewandowski and Beyenal (2008) and Videla and Herrera (2005) also describe that microorganisms can change the structure of a biofilm, which could lead to detachment of the biofilm and induces corrosion. In addition Videla and Herrera (2005) assign the increase in conductivity of the liquid movement as an corrosion inducer.

Another way for microorganisms to increase corrosion is by inactivation of corrosion inhibitors (Zarasvand and Rai, 2014). Due to the biofilm attached to the metal surface, corrosion inhibitors are not able to reach the metal. The biofilm could also consume corrosion inhibitors as nutrients. The formation of corrosive substances such as acids could increase corrosion rates (Zarasvand and Rai, 2014). Zarasvand and Rai (2014) and Little and Lee (2007) describe that changes in the molar ratios of aggressive ions to inhibiting ions can increase or induce corrosions. Alternation of anion ratios is possible because of competitive uptake of the anions by adsorption or ion exchange.

The major bacteria that are involved in increasing corrosion rates are the sulphate-reducing bacteria, the manganese/iron oxidizing bacteria, the iron-reducing bacteria and the acid-producing bacteria (Zarasvand and Rai, 2014). The sulphate reducing bacteria contribute to 50% of all instances of corrosion and are therefore extensively described in Chapter 3 (Hamilton, 1985).

### 2.2.2. Reducing corrosion rates

Microorganisms can not only increase corrosion rates, they are also able to reduce corrosion rates. Videla and Herrera (2005), Zarasvand and Rai (2014) and Lin and Ballim (2012) describe different modifications that could reduce corrosion rates such as:

- Form new or stabilize pre-existing passive films
- Inhibiting the action of corrosive substances
- Decreasing the corrosive action of the medium
- Reducing the cathodic reaction due to the consumption of a cathodic electron acceptor
- Reducing the rate of anodic oxidation and decreasing the ionic conductivity of the solution

CO<sub>2</sub> can influence the corrosion process by forming passive layers of minerals on the metal surface. Because these passive films were found in previous research done by Phd student Michael, this process will be discussed in Chapter 4.

Besides the properties of the corroding metal and the microbial structure there are also environmental factors influencing the corrosion rates (Lewandowski and Beyenal, 2008; Hernandez et al., 2012; Kehler et al., 2001). These environmental factors are:

1. pH
2. Temperature
3. Pressure
4. Solution Chemistry
5. Flow
6. Metallurgy of the steel
7. Surface films
8. Electrolyte composition and molar ratios of anions

The influence of the environmental factors on corrosion rates are discussed in the coming chapters.

## Inducing anaerobic corrosion

As described in Chapter 2 the sulphate reducing bacteria are the main microorganisms inducing corrosion. This chapter will first explain what sulphate reducing bacteria are and how they survive according to the environmental factors described at the end of Chapter 2. The second part of this chapter will describe the chemical process of sulphate reducing bacteria in the soil.

### 3.1. Sulphate Reducing Bacteria

Sulphate reducing bacteria gain energy by the reduction of sulphate to hydrogen sulphide. SRB are only able to survive in anoxic environments (Hamilton, 1985). Because there is always a little oxygen dissolved in water, the SRB are only able to live in the anaerobic parts of biofilms. A biofilm is structured in such way that aerobic microorganisms live in the outer part and anaerobic microorganisms live in the inner part (Figure 3.1). SRB live in pH neutral environments, pH ranges between 4 and 9 (Peng and Park, 1994). At a pH value of 7 the optimum temperature for growth of SRB is around 36 degrees Celsius (Al-Zuhair et al., 2008). Because in the soil, temperatures are smaller, the sulphate reducers grow slower.

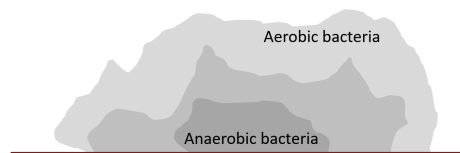
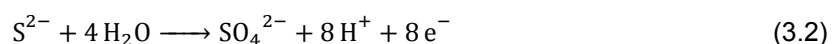
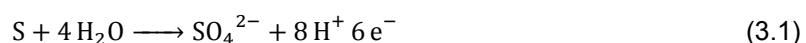


Figure 3.1: Aerobic and anaerobic bacteria in a biofilm

Sulphate reducers are usually found in clay soils (Videla and Herrera, 2005). The sulphate could be present in the soil or other bacteria could form sulphate first. The sulphide ( $S^{2-}$ ) oxidizing bacteria and the sulphur ( $S^0$ ) oxidizing bacteria are able to form sulphate. Figure 3.2 shows the process how sulphide and sulphur oxidizing bacteria can form sulphate and how sulphate can be reduced to sulphide by SRB. The left circle can not continue forever, because for each transition energy is lost. In the end there would be not enough energy available to continue the circle. With more sulphide or sulphur than sulphate in the soil, these oxidizing processes could affect the electrochemical reaction and accelerate corrosion (Zarasvand and Rai, 2014). The oxidizing reactions for sulphur and sulphide are respectively given in Reactions 3.1 and 3.2.



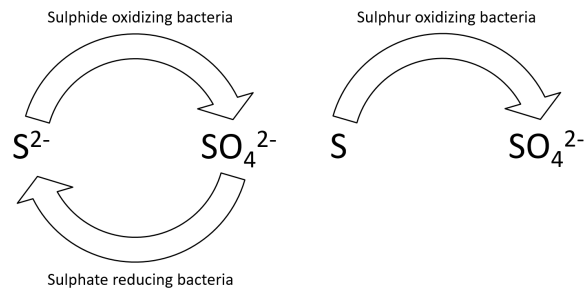


Figure 3.2: Bacteria oxidizing sulphide and sulphur and reducing sulphate

How SRB influence the corrosion process has been researched in the past 100 years. Enning and Garrelfs (2014) and Videla and Herrera (2005) both give an overview of the discoveries of the late century. Initially Kühr and van der Vlugt (1934) proposed a theory describing cathodic hydrogen as the electron donor. In this case molecular hydrogen is oxidized to atomic hydrogen, serving as electron donor. The microbial consumption of  $H_2$  was assumed to increase the corrosion rates. Later research questioned this theory and found that indeed hydrogen could serve as the electron donor, but not alone. the process would be too slow to increase corrosion rates. Also it was discovered that not the consumption of  $H_2$  increased corrosion rates, but the formation of hydrogen sulphate was the catalyser. Hydrogen sulphate reduces the pH and therefore increases corrosion rates. Besides hydrogen other organic electron donors are needed at the same time, such as lactate or acetate (Cord-Ruwisch, 2000). In the seventies microbial corrosion was also explained by reaction between sulphide and iron directly.

This results in three possibilities for SRB to contribute to corrosion processes.

1. Direct corrosion with  $Fe^{2+}$  as the electron donor
2. Indirect corrosion with  $H_2$  as the electron donor
3. Indirect corrosion with organic compounds as the electron donor

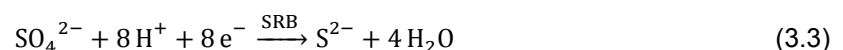
Different SRB have preferences for indirect or direct corrosion (Enning and Garrelfs, 2014). Autotrophic SRB use  $H_2$  as electron donor, while heterotrophic SRB use organic compounds as electron donor (Liamleam and Annachhatre, 2007).

### 3.2. Corrosion process

In this section the three ways of increasing corrosion rates by SRB will be discussed. First the direct corrosion process, which leads immediately to the corrosion product  $FeS$ , will be explained. In subsection 3.2.2 both the corrosion with  $H_2$  and with organic matter will be explained. These three processes may occur simultaneously but at different rates (Enning and Garrelfs, 2014).

#### 3.2.1. Direct corrosion

In iron corrosion the corrosion product is iron sulphide. This corrosion process can be described with four different reactions. The first reaction is the oxidation of iron, which takes place at the sheet pile surface. The oxidation of iron has already been given in Reaction 2.1. The second reaction that takes place is the reduction of sulphate. The sulphate reducers need 8 electrons in order to reduce sulphate to sulphide. This means that per mole sulphate reduced, four moles iron should be oxidized. Besides the electrons also hydrogen is needed, which is available in the soil by the dissolution of water. Reaction 3.3 shows the cathodic reaction reducing sulphate.



One of the ferrous iron molecules from equation 2.1 precipitates with the sulphide produced by the SRB. The total reaction is given in Reaction 3.4.



In this process, only one mole iron is able to precipitate with the sulphide. There are different options for the other three moles of iron. For example, the iron could precipitate with other free sulphide molecules that are available in the soil. Another possibility is that the iron could react with carbonate, which will be discussed in the next chapter. Furthermore the iron could react with other molecules present in the soil.

In Figure 3.3 the previously described process is schematized. At the sheet pile surface iron oxidizes and releases its electrons. The sulphate is reduced using these electrons and the protons present in the soil. The formed sulphide and ferrous iron precipitate as iron sulphide on the sheet pile surface. The corrosion occurs at the location where the iron is oxidized.

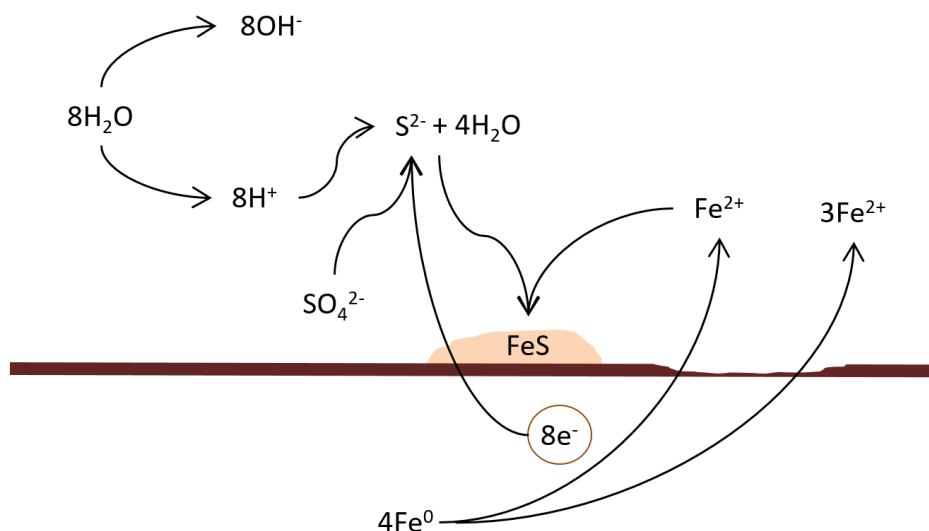


Figure 3.3: Direct corrosion process

Due to the formation of the corrosion product at the metal surface heterogeneities at this surface occur. The  $\text{FeS}$  precipitations on the metal surface accelerates the corrosion by creating a new active-passive cell. The iron below the layer of  $\text{FeS}$  is initially relatively safe to corrosion, but when the  $\text{FeS}$  layer breaks down the iron below the surface becomes active and oxidation goes really fast (Lewandowski and Beyenal, 2008; Videla and Herrera, 2005).



Figure 3.4: A passive active cell due to  $\text{FeS}$  precipitation

### 3.2.2. Indirect corrosion

When corrosion occurs indirect, iron is not the electron donor for the sulphate reducers. There are two other options for the electron donor. Heterotrophic SRB use organic matter as electron donor, while autotrophic SRB use  $\text{H}_2$  (Liamleam and Annachhatre, 2007). Both cases will be discussed further.

#### $\text{H}_2$ as electron donor

Autotrophic SRB use  $\text{H}_2$  as the electron donor. The oxidation of  $\text{H}_2$  is given in equation 3.5. Per mole reduced sulphate, four moles of hydrogen need to be oxidized.



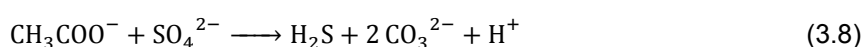
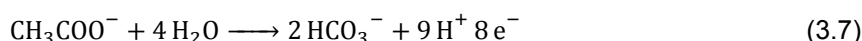
Combining Reaction 3.3 and Reaction 3.5 results in Reaction 3.6.



In this case the oxidation of iron occurs due to another redox reaction. For instance the aerobic corrosion process described in Chapter 2. The oxidized iron that is present in the bulk can now react with the formed sulphide from Reaction 3.6 and precipitate as FeS shown in Reaction 3.4.

#### Organic compounds as electron donor

There are multiple organic compounds in the soil available to act as electron donor. As an example acetate<sup>-</sup> is used as electron donor. The oxidation of acetate<sup>-</sup> is given in Reaction 3.7. This reaction releases 8 electrons. Combining the oxidation of acetate<sup>-</sup> (Reaction 3.7) and the reduction of sulphate (Reaction 3.3) results in Reaction 3.8.



The iron on the sheet pile surface oxidizes and the H<sub>2</sub>S reduces forming FeS. This process is schematized in Figure 3.5. The iron is oxidized at the metal surface releasing 2 electrons. The H<sub>2</sub>S is reduced using the 2 electrons from the iron oxidation. FeS and H<sup>+</sup> are formed. The reduction of H<sub>2</sub>S is given in Reaction 3.9. H<sub>2</sub>S is a powerful cathodic and anodic reactant which reacts directly with the iron surface (Enning and Garrelfs, 2014). By reaction with iron, protons are released. These protons acidify the area and therefore increase the anodic reaction of iron. The two protons from Reaction 3.9 can also be reduced to H<sub>2</sub> as shown in Reaction 3.10. So H<sub>2</sub>S is also a cathodic reactant. The reduction to H<sub>2</sub> is possible, but does not occur often. Combining Reaction 3.9 with Reaction 2.1 results in Reaction 3.11.

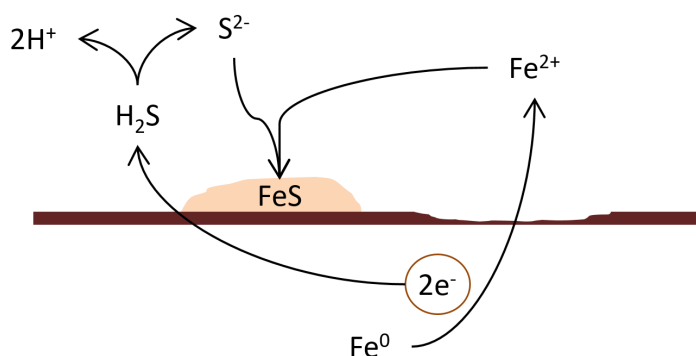
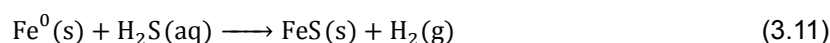
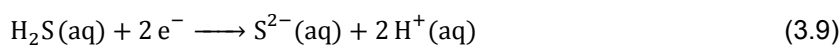
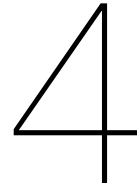


Figure 3.5: Precipitation of FeS with Fe as electron donor and H<sub>2</sub>S as electron acceptor

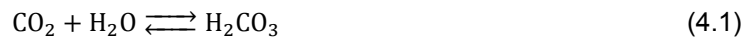


## Preventing anaerobic corrosion

In Chapter 2 multiple microbial mechanisms were given that could prevent corrosion. In this chapter the focus will be the formation of a protective layer of iron carbonate. The focus is chosen to be on this mechanism, because it was noticed in previous research by Phd student Michael.

### 4.1. CO<sub>2</sub> corrosion

A layer of iron carbonate forms a diffusion barrier for species involving corrosion. A protective iron carbonate layer can be formed by carbon dioxide influenced corrosion. In this process carbon dioxide is the carbon source and iron the electron donor. There are multiple options for the electron acceptor, which are discussed in the next section. CO<sub>2</sub> is mostly found in peat layers, where it is formed when organic matter decays. The CO<sub>2</sub> gas that is released in the soil hydrates with water to form carbonic acid. The dissolution reaction is given in Reaction 4.1.



According to reactions 4.2 and 4.3 the carbonic acid is in equilibrium with bicarbonate and carbonate. Which of these carbonate forms is dominant in the solution depends on the pH value. Figure 4.1 shows the carbonate forms that are dominant at different pH values. Because iron is only able to precipitate with HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup>, the formation of a protective layer is more likely to occur at high pH values (Hernandez et al., 2012).



Hernandez et al. (2012) examined the effects of temperature on corrosion of steel immersed in a 3 % wt NaCl solution saturated with CO<sub>2</sub>. The formation of an iron carbonate layer only occurred at high temperatures. At temperatures below < 60°C the layer is not able to adhere to the surface. In soils where the temperatures are usually low, at least much lower than 60°C, these layers were also found. The experiment was performed in low pH values (pH of 3.9) so it is more likely that the pH has a larger influence than temperature. With higher pH values and lower temperatures the iron carbonate layer is able to adhere

### 4.2. Corrosion process

The formation of an iron carbonate layer is a precipitation reaction. This means the iron has to be oxidized first. There are two main options. The iron could react with the oxygen at the top of the sheet pile wall, as has been discussed in Chapter 2. The other option is that the iron reacts with electron

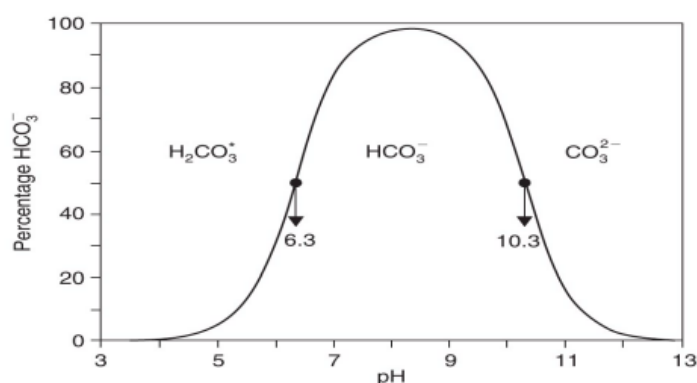
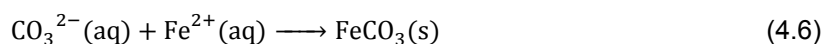
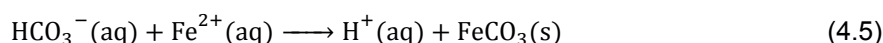


Figure 4.1: Percentage of  $\text{HCO}_3^-$  of total dissolved carbonate as a function of pH (Appelo and Postma, 2005)

acceptors in the soil. This could for instance be the hydrogen ions that come free after dissolution of  $\text{H}_2\text{CO}_3$  and  $\text{HCO}_3^-$  or the  $\text{H}^+$  that is always present in water. The reduction reaction of hydrogen ions is shown in Reaction 4.4.



The formation of the iron carbonate layer can be formed by reaction of oxidized iron with bicarbonate or carbonate. Both processes are given in reactions 4.5 and 4.6.



The formation of the iron carbonate layer is shown in Figure 4.2. Iron is oxidized using oxygen as electron acceptor. The hydrogen ions are released from the bicarbonate. The oxidized iron reacts with the carbonate forming the iron carbonate layer.

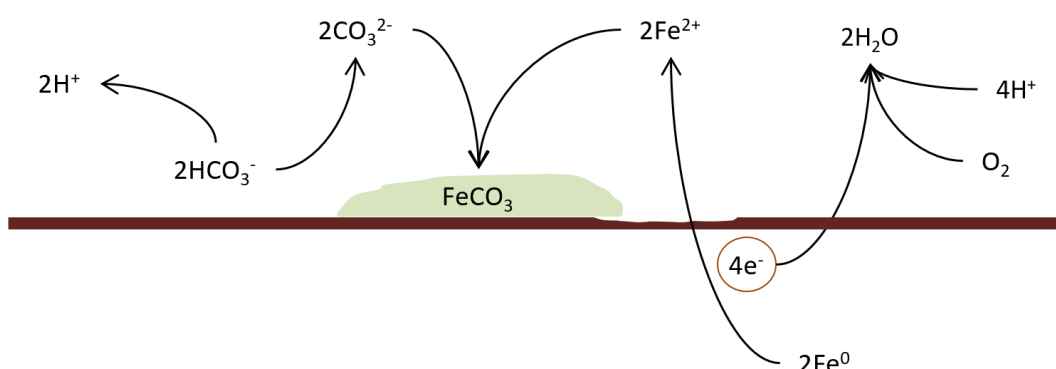


Figure 4.2: the formation of an iron carbonate layer

#### 4.2.1. Protectiveness of the layer

The formation of an iron carbonate layer is not a guarantee that the iron surface is protected. there are three things that could influence the protectiveness of the layer. All three will be discussed briefly.

### Concentration $Fe^{2+}$

From Reaction 4.5 the equilibrium constant can be defined as given in Reaction 4.7. This reaction shows that  $FeCO_3$  precipitation is a function of pH,  $Fe^{2+}$  and  $HCO_3^-$  concentrations. The influence of the pH was already described. If the  $Fe^{2+}$  concentration increases and there is not enough (bi)carbonate available, the  $Fe^{2+}$  ions stay in solution. This leads to acidification. Because of the acidification the protective layers become less protective (Nesic et al., 1996; Crolet et al., 1998).

$$K = \frac{[H+]}{[Fe^{2+}][HCO_3^-]} \quad (4.7)$$

### Influence of carbon

A sheet pile does not consist of 100% iron. If it is an alloy with a small amount of carbon, the formation of  $Fe_3C$  could harm the protective layer. When the iron oxidation reaction goes faster than the precipitation reaction the iron in the bulk increases. The formation of the  $Fe_3C$  depends on the microstructure of the steel. The steel from the experiment by Hernandez et al. (2012) consisted of a microstructure of ferrite and  $Fe_3C$ . The corrosion process etched out the  $Fe^{2+}$  ions from the structure, leaving  $Fe_3C$  behind. The internal acidification caused by the  $Fe_3C$  prevents precipitation of iron carbonate.

### Influence of Calcium

Esmaeely et al. (2013) studied the influence of calcium on the corrosion of steel in saline aquifers under low  $CO_2$  partial pressures. For the cases with low  $Ca^{2+}$  concentrations the formation of a protective layer was not influenced. However for larger concentrations of 1000 ppm or higher a mixed iron and calcium layer was formed and corrosion rates did not decrease. The additional formation of  $CaCO_3$  leads to acidification, resulting in more oxidation of iron. Due to the precipitation of  $CaCO_3$  the solution gets under saturated with  $FeCO_3$ . The concentration of Calcium decreases and when all possible  $CaCO_3$  is formed, the iron reacts with the remained carbonate. After the saturation level of iron carbonate is reached, the concentration of  $Fe^{2+}$  ions in the solution increase.



# 5

## Corrosion in soils

In this chapter the information of Chapter 3 and 4 will be related to different soil types and environments. A soil profile is chosen and elucidated in the first part of this chapter. The different microorganisms present in each soil layer will be determined. In the second part of this chapter the interaction between the different chemical species will be discussed.

### 5.1. Soil profile

The soil profile used is given in Figure 5.1. The profile is chosen in such way that the three most common soils in the Netherlands are present. From top to bottom it consists of clay, a small sand layer, peat and then the deeper sand layer. There is no relation to a real soil profile.

The chemical species most influencing corrosion are: oxygen, sulphate, carbon dioxide, nitrate and water. The concentration of these species in the different soil layers are shown in Figure 5.2.

The oxygen concentration is indicated with the blue line. The oxygen concentration line is based on a graph of the concentrations in Lake Michigan given in the course *Environmental Geotechnics*. Lake Michigan contains a lot of organic matter. Therefore this region is comparable to the western part of the Netherlands. The graph can be found in Appendix A. At the surface level the oxygen concentration is 100%. The concentration reduces fast when going deeper into the soil. Because of the low solubility of oxygen in water, the oxygen concentrations decreases when the water level is reached.

The water level is indicated in the soil profile at the left side of Figure 5.2. Below the water level the soil is fully saturated so the concentration is 100%. Above the water level the concentration decreases slowly, due to capillary rise.

The  $\text{CO}_2$  concentration is indicated with the orange line. The concentration is the highest in peat layers, where organic matter decays. The formed  $\text{CO}_2$  gas moves upwards through the soil. Therefore the  $\text{CO}_2$  concentration reduces slowly in the sand layer above the peat layer. Due to the outflow flux of  $\text{CO}_2$  gas at the surface, the soil does not become saturated with  $\text{CO}_2$ . At the top of the soil  $\text{CO}_2$  penetrates the soil for example due to acid rain. Also root respiration contributes to the  $\text{CO}_2$  concentration at the surface.

The sulphate concentration is the highest in clay. In sand and peat the concentrations are generally low. Casagrande (1987) investigated the concentrations of sulphate in peats from the Okefenokee

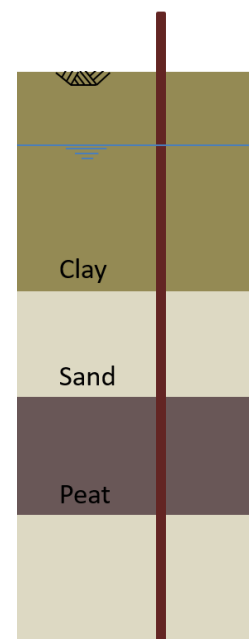


Figure 5.1: Chosen soil profile

(freshwater) and Everglades (marine) swamps. He found out that generally marine environments have a higher sulphur content than freshwater-influenced peats. In low sulphur freshwater peat, the concentration of sulphate is about 2%. In high sulphur marine peat, the concentration of sulphate is about 7% (Casagrande, 1987).

Nitrate concentrations in soils are high in clays and silts. Coarser soils often lose nitrates due to leaching. Based on the graph from the course *Environmental Geotechnics* the nitrate concentration is determined. After oxygen, nitrate is a wanted electron acceptor. Therefore nitrate concentrations reduce quite quickly after the oxygen concentration has dropped.

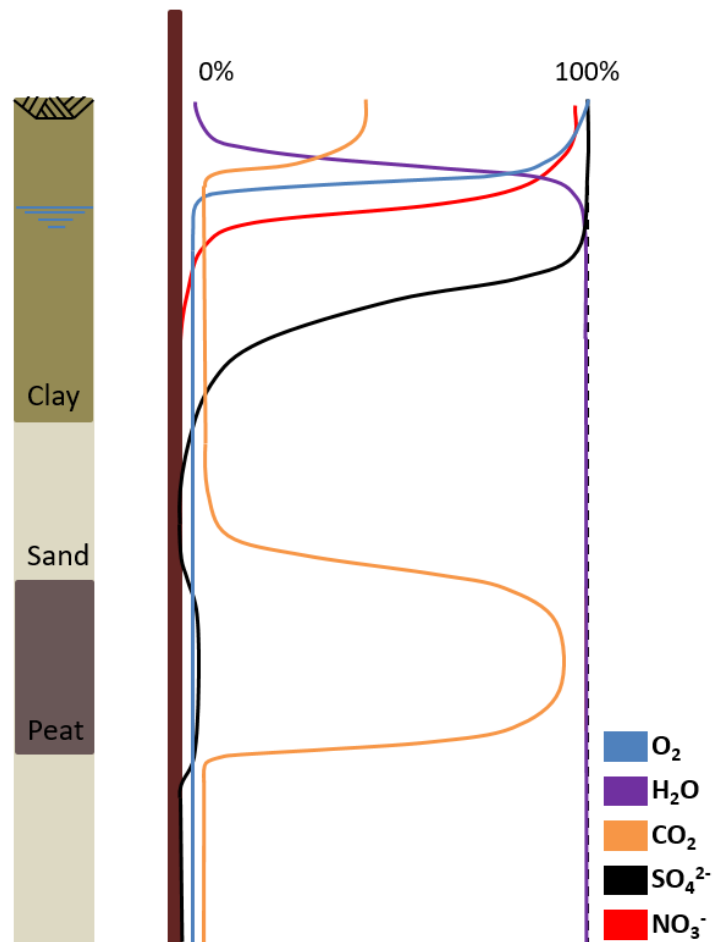


Figure 5.2: Potential of chemical species influencing corrosion in different soil layers

## 5.2. Electron acceptor preference

The soil type defines which reactions are possible. But the fact that a reaction is possible does not mean that it also takes place. Other chemical species in the surrounding are also relevant. Reactions that gain a lot of energy have a preference to occur. Therefore it could be that species are overruled by others. Figure 5.3 shows the electron acceptors from highest to lowest energy potential, when they have the same electron donor.



Figure 5.3: Electron acceptors in order from most energy released (left) to least energy released (right)

# 6

## Conceptual model

This report concludes with the conceptual model that could be made from the findings of the previous chapters. This chapter contains a description of the areas where corrosion and corrosion inhibition takes place and why. Figure 5.2 is used as a guideline. The soil profile is discussed from top to bottom with its conclusions and comments. Figure 6.1 shows the conceptual model.

### 6.1. The model

The top part of the clay layer is above the water level. Here aerobic corrosion occurs. Iron reacts with oxygen forming  $\text{Fe}(\text{OH})_2$ . The oxygen can also influence the oxidation processes deeper in the soil. The oxygen at the top is reduced to water, while down into the soil iron is oxidized. This results in a lot of  $\text{Fe}^{2+}$  ions around the sheet pile. These iron ions could precipitate with other species in the soil, if they are available. One of the downsides of high  $\text{Fe}^{2+}$  concentrations was discussed in Chapter 4. Larger concentrations of  $\text{Fe}^{2+}$  ions acidifies the area, making it less possible for iron ions to precipitate with carbonate. So the reaction of iron with oxygen makes it less possible to create protective films deeper in the soil.

Going down a little, to the clay layer below the water level, a sulphate rich environment is reached. Sulphate reducing bacteria are present in large numbers. The corrosion product  $\text{FeS}$  is formed. Chapter 5 described that sulphate is a less wanted electron acceptor than nitrate. If nitrate is present in the soil, the growth of heterotrophic nitrate-reducing bacteria (hNRB) is stimulated (Zaravand and Rai, 2014). These hNRB are able to reduce nitrate to nitrite, nitric oxide, nitrous oxide and nitrogen. They can use acetate<sup>-</sup> as their electron donor. The hNRB and SRB compete for the same carbon source. Because more energy is gained for the nitrate reduction, nitrate reduction will beat sulphate reduction (Thauer et al., 1977). In the top of the clay layer nitrate is present. Therefore SRB are not able to react with the iron and the steel surface is relatively safe.

In the sand layer few microorganisms are able to survive, because there is not much energy available. However chemicals from the peat and clay layers can move through the groundwater to the sand layer. Therefore some cathodic reactions could take place and corrosion products form. In addition the iron is able to oxidize, because of oxygen reduction at the top of the sheet pile. Therefore it is expected that the  $\text{Fe}^{2+}$  concentration in the sand is high.

Further down in the peat layer the concentration of  $\text{CO}_2$  is very high. The production of an iron carbonate layer is possible here. The  $\text{CO}_2$  gas moves upward, so the iron carbonate layer can also be formed in the sand layer just above the peat layer. The protectiveness of the carbonate layer depends on the concentration of  $\text{Ca}^{2+}$ , carbon and  $\text{Fe}^{2+}$  as described in Chapter 4. The sulphate reduction is low, but corrosion by SRB is possible. In the peat layer both processes are expected.

### 6.2. Remark

One remark has to be made about the description above. In this case a perfect homogeneous soil layer with homogeneous groundwater chemistry is assumed. However in reality this is not true. Therefore

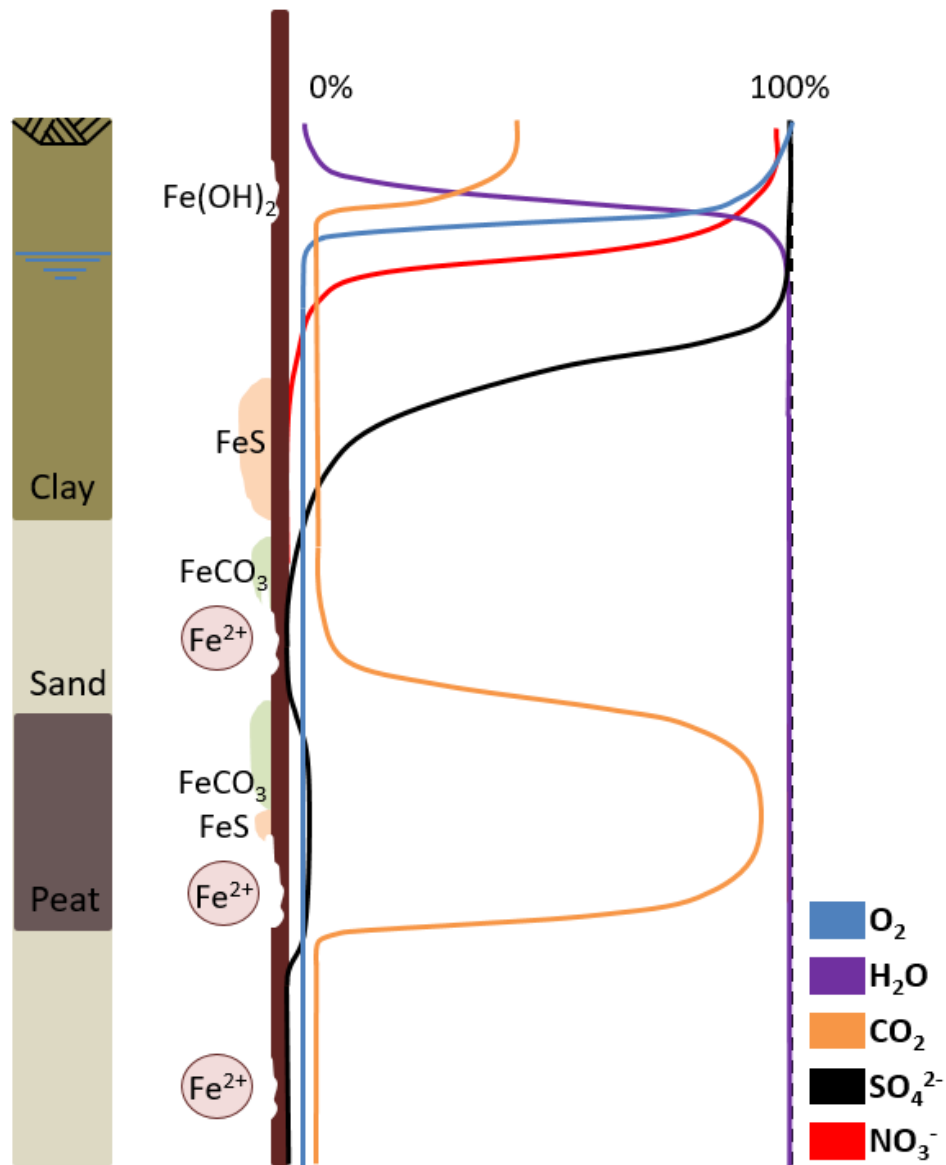


Figure 6.1: Conceptual model describing the areas where corrosion occurs and where corrosion is inhibited

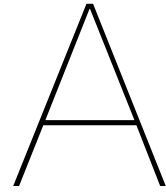
it is not possible to say at which location corrosion occurs or does not occur. If at some area the concentrations are out of balance this influences the corrosion rates.

For example, at the top of the clay layer below the water level we assume no corrosion to occur. But if the nitrate concentrations vary and are low at specific parts, the SRB are able to do their work and corrosion occurs. Also the concentration of  $\text{Ca}^{2+}$  ions can differ in space, leading to areas where  $\text{CaCO}_3$  forms (high  $\text{Ca}^{2+}$  concentration) or where  $\text{FeCO}_3$  forms (low  $\text{Ca}^{2+}$  concentration).

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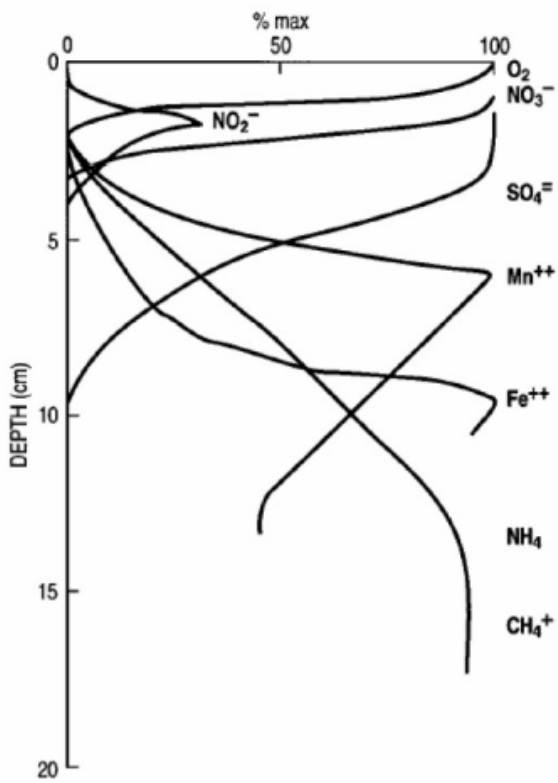
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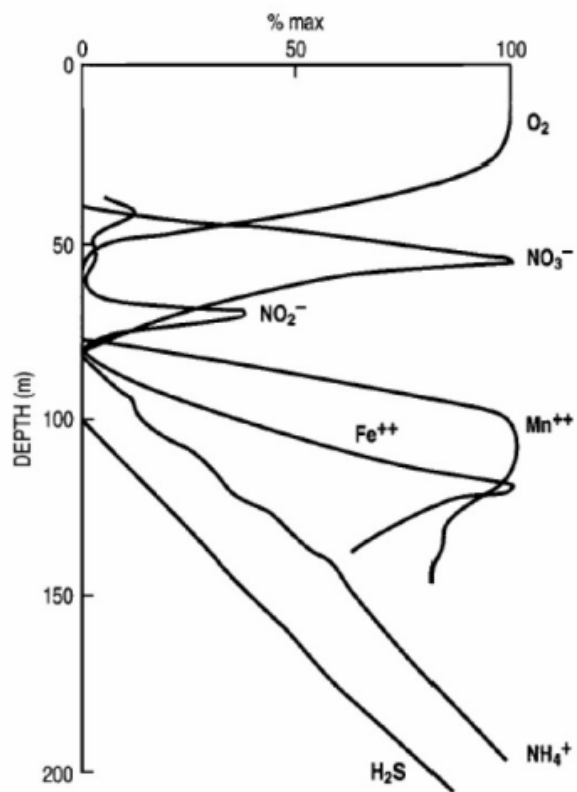


# Lake Michigan

This Appendix contains the graph of the chemical species and there concentrations at different depths of Lake Michigan.



Lake Michigan Sediment



Black Sea

Figure A.1: Concentration of different chemical species over depth at Lake Michigan and the Black Sea