



Rapport

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Projekt
SmartInfra

Microbiologically influenced corrosion

Smart monitoring of infrastructure asset health and performance in drinking water distribution systems

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Acknowledgment

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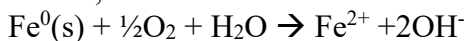
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1. Background & What is MIC

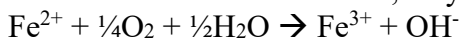
Corrosion in the drinking water distribution system (DWDS) is a common, yet a very costly problem. Cast iron pipes have been used for over 500 years although plastic is most commonly used in modern day when building new pipes (McNeill & Edwards 2001). Internal corrosion of iron pipes is ubiquitous in DWDS (Sun et al. 2014; Lin et al. 2001). It causes loss of mass of the functional pipe, leading to breakage or worsening the function of pipes (McNeill & Edwards 2001). Furthermore, the water quality flowing through may deteriorate (Sun et al 2014). Iron corrosion product release from pipe walls, “red water”, is one of the most common customer complaints of drinking water (Sun et al 2014; McNeill & Edwards 2001). Particles that diffuse into water may sediment in stagnant water and later spread upon increased water flow, causing discolored water in customer taps (Svenskt Vatten P115). Particles that cause discoloration or turbidity may however originate from the water itself, loose deposits. It may not be caused by corrosion of pipe material (Vreeburg et al. 2008).

The definition of corrosion is an undesirable chemical reaction between a material and its environment. Metal corrosion is deterioration of metals or alloys caused by the action of air, moisture or chemical reaction on their surface. The corroded surfaces may be exposed to an unfavorable chemical or electrochemical environment. It’s a redox reaction (reduction-oxidation reaction) where electrons are moved from one atom (reducing agent) to another (oxidizing agent), in this case from the metal to oxygen or water. The number of moved electrons depends on how much the metal is oxidized (which charge the metal ion ends up with). The most common iron ions are +2/+3 charged whilst the most common copper ions are +1/+2 charged. Electrons that are moved from metal reduces oxygen and together with water it forms hydroxide ions. Metal ions diffuses in water whilst electrons are transported through the pipe material.

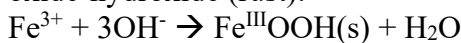
In iron, the first redox reaction is:



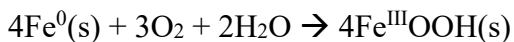
When metal ions are oxidized, they react with hydroxide ions and form metal hydroxide.



Iron is often oxidized to 3-charged ions beforehand and form almost insoluble iron (III) oxide-hydroxide (rust):



The overall chemical formula of this is:



The amount of iron atoms are not increased in rust build-up but additional atoms that bind in to form $\text{Fe}^{\text{III}}\text{OOH}$ creates the build-up inside distribution pipes.

Corrosion cause failure in metallic structures that are essential for drinking water distribution. Metal pipes may deteriorate due to build-up of iron, inducing loss of pressure and altered flow in the distribution (Figure 1). The corrosion products that build up on pipe walls may function to inhibit further corrosion but extensive build-up alters water-flow (Svenskt Vatten P115). Such a thick build-up may also function as reservoir for a wide array of microorganisms, some potentially harmful, in biofilm (Xin et al. 2023; Wingender & Flemming. 2011). Concrete and cement structures with metal reinforcement may break due to corrosion. Furthermore, iron may be released into bulk water and cause aesthetic

problems. Corrosion frequently occurs in copper pipes as well, causing high levels of copper in the water (Galarce et al. 2020).

There are many factors in drinking water that influence corrosion: pH, source water, salinity, oxygen level, water hardness and flow speed. If the water has a very low flow rate or is completely stagnant (even periodically stagnant), the risk for corrosion is dramatically increased. Drinking water analyses at Norrvatten have shown that iron concentration, turbidity and color are often connected because they are all based on spectrophotometry. If an analyzed water sample is colored yellow to the eye, but does not contain high levels of iron, the reason is a high content of organic matter. There are multiple corrosion indices that may be used to calculate how corrosive or scaling a drinking water is. A few examples are the Langelier-, Ryzener-, Puckorius-, Aggressive and Larson index (McNeill & Edwards 2001; Yousefi et al. 2018; Shahmohammadi et al. 2018).

Most drinking water treatment plants utilize addition of lime or lye in order to increase the pH of the finished water. Furthermore, carbon dioxide (CO₂) is often added for additional alkalization. This is done to increase the water's ability to resist acidification. Hydrogen carbonate and carbonate ions can adsorb hydrogen atoms. Additionally, alkalization is done so that bicarbonate (HCO₃⁻) forms iron carbonate (Fe^{II}CO₃) or calcium carbonate (CaCO₃), which protects the inner pipe surface, inhibiting corrosion. An appropriate pH-value in finished drinking water should exceed 8.0 and is often set at 8.4 and not deviating from that significantly. Alkalinity is measured in mg hydrogen carbonate / liter and should exceed 60 mg/l. Fewer customer complaints have been reported when alkalinity is above 60 mg/l (McNeill & Edwards 2001). If the DWDS is extensive, it should instead be 80 – 100 mg/l. Too high levels of alkalinity, however, is undesirable as corrosion rate on copper material may increase.



Figure 1: Cast iron pipe that was installed in 1910 in Norrvatten's DWDS.

Corrosion is a frequently occurring phenomenon at multiple locations in Norrvatten's drinking water distribution system (DWDS). In October 2022, damage caused by corrosion was discovered in the pipe system in Ulriksdals ground water works, where weldings (svetsar) and flanges (flänsar) connect. The material on which the damage occurred has a high class of corrosion-resistance (syrafast 1.44.32). Current working hypothesis, formulated by Bo Berghult, is that the reason is high concentration of chloride (100 mg/l) and stagnant

water causing crevice corrosion. Chloride is either negatively charged ions (Cl^-) or chlorine ion bound to a molecule with ion-bonding (e.g. NaCl, KCl, etc.).

Additionally, iron pipes throughout the DWDS have to be renewed regularly as they can have high amounts of iron build-up. One last example of Norrvatten's corrosion challenges is the function of valves. Norrvatten had to lodge a claim on a valve manufactured by AVK (Århus, Denmark) that was placed in Sjöändan due to corrosion damage, despite its thorough resistance. Normally, this can only occur if the water has a high concentration of chloride.

Corrosion is a well-known phenomenon but it is less known that the reason can be microorganisms. One of the most primitive types of living metabolism is connected to iron. This phenomenon has therefore been present long before multicellular organisms. Microbiologically influenced corrosion (MIC), or bio-corrosion, can be explained as "corrosion affected by the presence or activity (or both) of microorganisms in biofilm on the surface of the corroding material". It can also be explained as "deterioration of metals caused by metabolism of microorganisms". The role of microorganisms in corrosion can be described as electrochemical catalysts (Starosvetsky et al. 2001). It is important to point out that MIC is not a new or separate type of corrosion, rather it induces "classic" corrosion.

Biofilm can be explained as a community of microorganisms that are attached to a surface. Bacteria are attached to and embedded in extracellular polymeric substances that was produced by bacteria. Iron pipes have been shown to allow much faster biofilm growth compared to plastic materials (Liu et al. 2014) In addition, iron pipes may host the highest bacterial abundance in biofilm, up to 45 times higher (Niquette et al. 2000). In order for MIC to occur, an active biofilm needs to be in contact with the metal surface. The biofilm changes the chemical environment, inducing an electrochemical reaction between microorganisms and the pipe material, enhancing the procedure (Kadukova & Pristas 2018). Overall, MIC has been estimated to cause about 20 % of all corrosion damages (on all metal structures) worldwide. It has been reported that biofilms may increase the rate of corrosion of pipe materials by up to 10,000 times. Corrosion build-up in pipes creates new niche environments that are suitable for microorganisms to inhabit (Batté et al. 2003).

2. Mechanism

A variety of MIC mechanisms are known and described but details are still unknown. A few examples of how microorganisms can enhance corrosion process are listed below (Kadukova & Pristas 2018). Microorganisms break the passive layer and stimulate anodic or cathodic reactions due to:

- Degradation of the passive layer
- Production of corrosive compounds such as sulfides, nitrites, ammonia and acids
- Consumption of protective coating layer
- Secretion of electrically active molecules
- Production of extracellular polymeric substances able to take up metal ions

MIC is a three-steps process. Step 1 is formation of biofilm, which is initiated immediately but can take months to years to be stabilized. Microorganisms attach a network of exopolysaccharides to the metal surface using strong chemical interactions. After attachment many other biological processes occur, such as bacterial regrowth. Step 2 in the MIC process

is when metabolic activity changes the environment on the metal surface. For example, pH and oxygen levels are lowered. The types of ions in these biofilm environments change throughout this process and the concentration of them as well, the electrochemical conditions. In research, the concept of electrochemically active biofilms is therefore increasing in interest. Local anodes and cathodes are formed. When two different metals are involved, the most precious of them form the cathode whilst the other is downgraded as anode. This is when step 3 occurs and corrosion takes place. Biocorrosion is an increase of electronic transfer in presence of biofilm. MIC is not limited to a single type of corrosion. MIC can cause localized deterioration: pitting, crevice, dealloying and under deposit. It can also accelerate galvanic corrosion, hydrogen cracking and stress corrosion.

Bacterial biofilms are naturally formed on every known surface. The presence of biofilm on metal surfaces in drinking water systems does not automatically mean corrosion is occurring. There is no scientific consensus whether biofilms enhance or inhibit corrosion. Some studies have found that biofilms can act as a protective layer, inhibiting corrosion, just like paint, enamel and lacquer. Corrosion is inhibited this way because iron ions cannot leave the metal surface. Other studies found results indicating the opposite, that biofilms greatly enhance the corrosion process. The most likely explanation is that the chemical environment, the biofilm properties such as composition, and the water properties are determining factors.

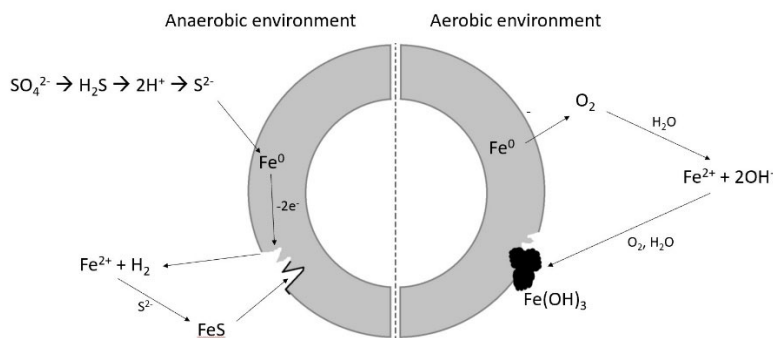


Figure 2: Basic principles of MIC mechanisms under aerobic and anaerobic conditions (derived from Kadukova & Pristas. 2018). Iron(II) sulfide in anaerobic environment and iron(III) hydroxide in aerobic environment.

3. Involved microorganisms

MIC, naturally, only occur when there are microorganisms present and diverse types of organisms may cause MIC. There are representatives from all 3 domains of life: bacteria, eukarya and archaea. Bacteria are perhaps most common but archaea and fungi have also been observed to cause corrosion using complex metabolism (Planý et al. 2021; Okorie & Chukwudi. 2021; Kadukova & Pristas 2018). There are numerous species that can affect metal. The composition of bacteria is an important factor for the metabolic processes taking place. Prokaryotic organisms that are involved in MIC are taxonomically diverse, meaning they can be found in various groups. Consequently, they may also possess vastly different metabolisms (Kadukova & Pristas 2018). The most common types of bacteria found at sites

of MIC are: sulphate reducers/oxidizers, acid producing and iron reducing/oxidizing. More information about these groups of bacteria is presented below and known species are listed. Furthermore, general chemical reactions of key metabolic processes are presented.

3.1. Sulfur reducing bacteria

The type of microorganisms that are most commonly found in MIC are sulfur reducers. There are both bacteria and archaea represented in this group, so they may be referred to as Sulfate Reducing Prokaryotes (SRP). As bacteria are more common, this text will focus on them (Sulfate Reducing Bacteria, SRB). They are the main MIC-concern of industrial operators (Kadukova & Pristas 2018). It has been estimated that SRB are responsible for more than 50 % of failures of buried pipelines.

SRB are often found in soils, sediments and water bodies (Wargin et al 2007). There are approximately 220 species that are divided into 60 genera. SRB are often described as a phenotypic group (based on their properties and metabolism), not genotypic (phylogeny). However, many sulfate reducers are found in phyla Thermodesulfobacteriota, Thermodesulfobium, Bacillota and Nitrospirota. Perhaps the most common species found in cases of MIC are *Desulfovibrio vulgaris*. Biocorrosion biofilms are often also dominated by genera *Desulfobacter*, *Desulfobacterium*, *Desulfotomaculum* and *Desulfobulbus*. They belong to the archaeobacteria group that are characterized by: peptidoglycan-free cell wall and specific cell membrane lipid composition, among other features (Wargin et al 2007). However, SRB are morphologically diverse: cells may form cocci, rods or curved shapes.

Cells size varies, as the length spectrum is around 1.3 – 9 µm (Wargin et al 2007). They thrive in oxygen-deficient environments such as stagnant plumbing systems, distribution systems and ground water (Wargin et al 2007). Most SRB are anaerobes and they are ubiquitous in anoxic habitats where they have an important role in carbon and sulfur cycles. Some are oxygen tolerant. UV treatment is an effective way to inactivate SRB if appropriate dose is utilized. UV dose of 400 J/m², which is Norrvatten's current dose, eliminates around 50 %. An increase to 600 J/m² would eliminate around 80 % (Wargin et al. 2007). SRB are capable of attacking a wide array of metals such as: stainless steel, aluminum, iron, nickel and copper due to their thermodynamic instability.

This group of bacteria obtain building components from carbon sources and energy through reducing sulfate to toxic hydrogen sulfide gas where sulfate is the terminal electron acceptor. SRB influence the taste and smell of drinking water by producing odorous hydrogen sulfide gas (Wargin et al 2007). The smell is very characteristic and it's obvious the compound is present when discovering black precipitation of ferrous sulfide (Wargin et al 2007). They also exchange oxygen for sulphate. Through their metabolism, the end products are iron hydroxide and iron sulfide.



Hydroxide is also formed, which drives the reaction further.

Sulfate can be analysed in a laboratory. SRBs are heterotrophs and can grow on yeast-peptone (Norrvatten's HPC method) although they cannot be identified using that analysis alone. Hydrogen sulfide is corrosive to metals like iron and steel.

SRB in ground water (and therefore also surface water, most likely) can be inactivated or removed with UV radiation and microfiltration. But odorous compounds, the result of their metabolic activity, is not removed with these techniques (Wargin et al 2007). GAC removes hydrogen sulfide but has limited effect on odorous compounds.

Sulfur oxidizing bacteria (SOB) may coexist with SRB. Species within genus *Sulfuricella* and *Thiobacillus* are also known to cause MIC (Sun et al 2014). Both SRB and SOB are able to draw energy from a synergistic sulfur cycle within the DWDS. A metabolic result of these organisms is deterioration of concrete and the reinforcing steel within.

3.2. Acid-producing bacteria

Some bacteria produce organic or inorganic acids as by-products in their metabolism. These acids may be directly involved in metal corrosion (Kadukova & Pristas 2018; Liu et al. 2007). Acid-producing bacteria are found in diverse phylogenetic groups.

1. An example is how sulfur-oxidizing bacteria such as *Acidithiobacillus ferrooxidans*, *Acidithiobacillus thiooxidans* and *Thiobacillus thioparus* oxidize sulfur compounds and form sulfurous acid (H_2SO_3) or sulfuric acid (H_2SO_4) (Liu et al. 2014).
2. Another example is how ammonia- and nitrite-oxidizing bacteria may produce nitric acid and nitrous acid.
3. Lastly, acetogenic bacteria have been found to enhance MIC in iron pipes by acetate in anoxic environments.

Inorganic acids is a complex phenomenon in biocorrosion. Salts that are formed by the acid-producing bacteria are soluble in water and no protective corrosion product layer is therefore formed. Furthermore, the pH is lowered, leading to dissolving of protective deposits such as calcium carbonate.

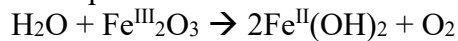
3.3. Iron reducing bacteria

Another important group of bacteria involved in MIC are iron reducing bacteria (IRB). Their role in MIC is however not yet completely mapped. In fact, IRB role in corrosion is a controversial subject (Kadukova & Pristas 2018). It is known that they are associated with elevated levels of iron, manganese and arsenic among other metals. In addition, IRB can create environments that benefit sulfate reducing bacteria, explaining why IRB are often found at sites that have been affected by MIC. Research on the field have given contradicting results. Some studies indicate that IRB can induce and enhance the corrosion process. According to those findings, iron reducers are likely to have an effect on corrosion by converting insoluble iron ions to water soluble ones. This action removes protective layers on the pipe surface and exposes it to corrosive medium. Other studies found that IRB straight up inhibited iron corrosion and iron release from pipes (Sun et al 2014). IRB are capable of reducing ferric iron to ferrous iron, which can inhibit iron corrosion. Aqueous solutions containing Fe^{3+} ions are often visibly colored. Fe^{2+} ions on the other hand does not significantly alter the aesthetics of water. IRB may therefore reduce aesthetic issues of drinking water with high iron content. Furthermore, IRB have been shown to favor the formation of the iron(II,III) oxide, magnetite (Fe_3O_4) that has been reported to protect iron

pipes from extensive iron release. Higher levels of magnetite has been positively correlated to higher abundance of IRB. A possible explanation is that IRB are capable of influencing by both inducing and inhibiting MIC, depending on the environment and conditions.

IRB derive energy by oxidizing ferrous iron. They reduce iron(III) by donating electrons to them, using them as a terminal electron acceptor, either through anaerobic respiration or fermentation. Using that type of metabolism, these bacteria can grow relatively rapidly under anaerobic conditions. In absence of iron, anaerobic cell growth is low. Their relative fitness is highest in neutral pH conditions, so acidic pH that generally enhances corrosion, does not benefit this group of bacteria (Cummings et al. 1999). IRB in ground water may convert iron compounds into ferrous iron (Fe^{2+}) and produce hydrogen sulfide gas (H_2S) in the process. The result is that groundwater may have an unpleasant odor.

A simplified metabolic reaction is:



If a biofilm contains water, iron oxide can undergo an electrochemical reaction. Iron hydroxide and oxygen is formed as the bacteria retrieve energy.

Some examples of known IRB are:

- *Thermoterrabacterium ferrireducens*
- *Bacillus infernus*
- *Desulfotomaculum reducens*
- *Clostridium beijerinckii*
- *Geothrix fermentans*
- *Desulfovibrio profundus*
- *Geobacter metallireducens*
- *Shewanella oneidensis*
- *Ferrimonas balearica*
- *Vibrio alginolyticus*
- *Ferribacterium limneticum*
- *Acidiphilium acidophilum*
- *Sulfurospirillum barnesii*
- *Deferribacter thermophilus*
- *Thermodesulfobacterium commune*
- *Thermotoga maritima*
- *Crenothrix*

3.4. Iron Oxidizing Bacteria (IOB)

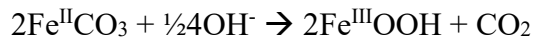
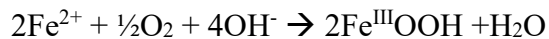
Iron Oxidizing Bacteria (IOB) are known to also cause MIC and speed up the rate. Red water events have been connected to high abundance of IOB. In such cases, the causative agent is often high concentrations of anions, in particular sulfate ions. Other factors involved in red water events are extended hydraulic retention time, insufficient disinfection residue, low levels of dissolved oxygen, low alkalinity, high temperature and high chloride concentration (Li et al. 2010). During red water events, the bulk water has high concentrations of ferrous iron that further enhance the growth of IOB. Residual chlorine

decreases due to reactions with ferrous iron. Chloramines are not particularly effective against IOB.

Formation of ferrous iron from elemental iron:



Fe^{2+} diffuses into water and $\text{Fe}^{\text{III}}\text{OOH}$ is formed:



IOB enhances oxidization of Fe^{2+} to Fe^{3+} . Iron oxidizers contribute to formation of $\text{Fe}^{\text{III}}\text{OOH}$ (Sun et al. 2014). Examples of IOB genera according to Sun et al. 2014 and Li et al. 2010 are:

- Acidovorax
- Gallionella
- Leptothrix
- Sphaerotilus
- Sideroxydans

4. Detection of MIC

It is near impossible to quantify MIC because it is difficult to distinguish MIC from “classical” corrosion. An estimation is that more than 50 % of corrosion in pipelines are due to microorganisms (Kadukova & Pristas 2018). In theory it is possible to detect and distinguish MIC using several different methods. It’s important to point out that none of these methods, to our knowledge, have been tested by Norrvatten or any other drinking water producer in Sweden. So the applicability is unknown, as well as it could be practically undoable. Detection of MIC is a challenging task. Some methods have been described for the purpose of detecting MIC but they rather detect general life or biological activity, so those methods have been left out. Below, some methods that are more specific for MIC are listed.

1. Electrochemical measurement. The chemical response to electrical stimulation, the reduction or uptake of electrons. In this way, corrosion and redox potential may be measured (Liu et al. 2007).
2. Surface analysis. Observing bacterial activity and their damage on metals. Fluorescence microscopy, atomic force microscopy, scanning electron microscopy, confocal laser scanning microscopy. A wide arrange of X-ray methods are also mentioned as options for surface analysis.
3. Lead acetate test. Identifies materials that contain sulfur (hydrogen sulfide H_2S).
4. Adenylyl sulfate reductase is an enzyme that reacts to sulfur compounds. Detects SRB.
5. A more advanced approach is molecular methods to detect specific microorganisms. This can be done with PCR techniques, sequencing or hybridization probe. The first two are perhaps more well-known than the last. Briefly explained, a hybridization probe is a sequence of nucleotides (DNA) that is radioactively or fluorescently

labeled. Upon binding to a matching nucleotide sequence on a solid surface, the radioactivity or fluorescence can be detected.

There are other methods that are known and used to detect corrosion in general, not necessarily MIC, such as linear polarization resistance tests.

There are kits for commercial use on the market such as Sig Sulphide. This test kit analyses corrosive sulphides that bacteria like SRB produce. The kit requires no additional equipment or education and is easily performed in field. A similar kit can be used in addition to Sig Sulphide, the Sig Nitrite. This kit analyses for Nitrite Reducing Bacteria that are involved in corrosion inhibitor depletion.

5. Protection against MIC and general corrosion

For industrial application, there are several methods of protection against MIC or reduce its effect. In drinking water systems, it is necessary to adjust the pH of finished product to around 8,2. This property of the water reduces risk for corrosion in general, as mentioned earlier.

Perhaps the most important method to avoid MIC is choice of material in DWDS as well as improved design. It's a complex issue however. Steel pipes are often covered by protective layers of zinc but it has been shown that microorganisms are capable of corroding even galvanized and stainless steel, in particular if the material has been welded (metallkompetens).

In addition to adjusting the water itself, it is common to build in coatings and linings in the components of the DWDS. These prevent corrosive electrolyte to come in contact with the electrodes of the metal. In this way, no electrochemical reaction takes place. Coatings and linings may also prevent microorganisms from attaching to the metal surface if they have hydrophobic properties.

Another method is cathodic and anodic protection. The corrosion potential is reduced by binding to an external anode, a sacrificial anode that is more active than the pipe material. In this way the electrochemical reaction is shifted from cathode and anode on the pipe material to cathode on the pipe material and an anode that has been built in.

In cases where corrosion has already developed or other strategies fail, mechanical- (brushing, pigging, water jet) or chemical cleaning (biocides and corrosion inhibitors) may be used.

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