Educational Article

Corrosion Control in Drinking Water Distribution Using Simple Methods

Part 3: Properties and Corrosion of Cast Iron and Steel

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Summary: Metals are valued for their excellent mechanical properties and are often used in the distribution of drinking water. Ferrous materials include unalloyed and low-alloy steels, as well as cast iron. However, iron is thermodynamically unstable in water and corrodes through hydrogen corrosion, whereby hydrogen ions are reduced to hydrogen. In the presence of oxygen, oxygen corrosion occurs, in which dissolved oxygen is reduced to hydroxide ions. In both processes, the metal oxidizes and either passes into the corrosion layer or dissolves in the water. However, low oxygen levels can also lead to quality issues, such as instationary corrosion, which causes rusty water. Many older pipes in the supply network are not protected against corrosion, so corrosion problems are still expected, especially if the water properties change. For unalloyed and low-alloy steels, as well as cast iron pipes without internal protection, the corrosion types "surface corrosion" and "pitting corrosion" are particularly significant. Cast iron must also consider the selective corrosion type "spongiosis," which can occur in older cast iron pipes with lamellar graphite ("gray cast iron") or in inadequately protected cast iron pipes with spheroidal graphite ("ductile cast iron"). Currently, cast iron pipes used for drinking water are well-protected with cement mortar on the inside and a zinc and polymer coating on the outside, which allows them to have a long service life.

Keywords: Alloys, cast iron, corrosion types, low-alloy steel, metals, phase boundaries, pitting corrosion, selective corrosion, surface corrosion, stainless steel.

Foreword: What is the purpose of this series of articles?

The aim of this series of publications is to provide information on the possibilities of corrosion control in the drinking water distribution network and in drinking water installations. The importance of corrosion to the materials used in drinking water distribution and to drinking water itself is presented, methods of investigation are explained, and possible corrosion control strategies are discussed. The goal is to provide water utilities, large consumers, and interested individuals with a deeper understanding of metal corrosion in drinking water.

1. Metals and alloys

Most elements in the periodic table are metals. The transition to semimetals and nonmetals occurs gradually. Some elements, such as phosphorus and arsenic, have nonmetallic, semimetallic, and metallic forms. They are called allotropes.

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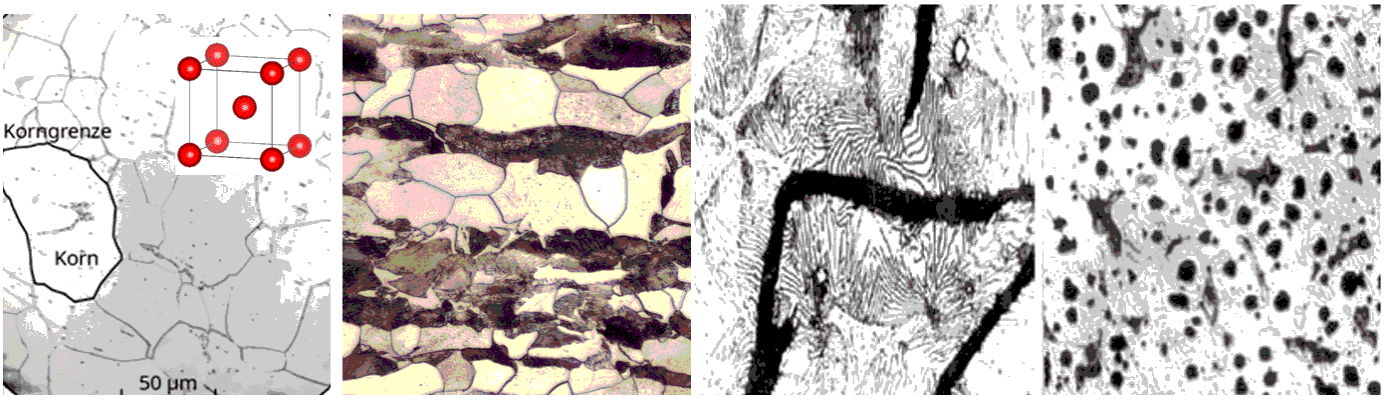
In general, metals and alloys are characterized by:

- **high electrical conductivity**, which decreases with increasing temperature;
- **high thermal conductivity**, which makes metals feel cool to the touch;
- **ductility (malleability)**, which allows them to be formed into thin sheets or wires;
- **a metal lattice** [1].

These properties are based on the fact that metal atoms are held together by metallic bonds in a lattice, and their outer electrons (valence electrons) are freely movable. Metal pieces are not single crystals but rather consist of **grains** or **crystallite**s separated by grain boundaries. Within these boundaries, the atoms are usually arranged uniformly. Depending on the metal and processing, the crystallites range in size from micrometers to several centimeters [2]. When the workpiece is polished and, if necessary, etched, it becomes visible that the crystallites are aligned differently (Figure 1a). Grain boundaries strongly influence the strength of the material, reducing electrical and thermal conductivity and promoting corrosion.

Iron is the second most abundant metal in the Earth's crust after aluminum. However, it is rarely used in its pure form; rather, it is used in the form of alloys with carbon and other metals, such as chromium and nickel. **Alloys** are macroscopically homogeneous materials consisting of at least two components, one of which is a metal that exhibits metallic behavior.



(a) **(b)** **(c)** **(d)**

Figure 1: (a) Grains and grain boundaries in iron with ferrite crystal lattice (insert), **(b)** Microstructure of an unalloyed steel with 0.35 % carbon with light ferrite grains and dark lamellar pearlite (laminar structure of ferrite and cementite) **, (c)** Cast iron with phase of lamellar graphite (black), **(d)** Cast iron with phase of spheroidal graphite (black) according to [3].

Alloys typically have a crystalline structure when the alloy components are present within the same crystal lattice [3]. However, different phases may also be present. For example, steel contains a pearlite phase (a laminar structure of ferrite and cementite) in addition to ferrite (body-centered cubic iron) (Figure 1b). Cast iron has a higher carbon content and an additional graphite phase that occurs in lamellar (Figure 1c) or spherical form (Figure 1d). The presence of different phases in alloys can lead to corrosion between grains, such as **spongiosis** in cast iron or stress corrosion cracking in stainless steel. The formation of localized elements is also promoted.

2. Iron materials in drinking water distribution

The use of metals in drinking water distribution has a centuries-old tradition. Cast iron pipes are especially common in distribution networks, while lead is common in drinking water installations. Metals are ductile, pressure-resistant, and easy to work with. Corrosion occurs comparatively slowly, meaning metal pipes can be used to transport

water. Under good operating conditions, cast iron and steel pipes installed in the 1930s are still in use today without any abnormalities. Early on, the corrosion problems of metal water pipes were well-known, particularly the tendency of cast iron pipes to supply brown water and the tendency of people in households with lead pipes to become ill.

2.1. Cast iron pipes in drinking water distribution

Cast iron is an iron-carbon alloy containing 2.5 to 5% carbon. Unlike steel, cast iron contains graphite in different shapes in addition to cementite [3]. Cast iron is easy to cast but harder and more brittle than steel. Depending on the wall thickness, its tensile strength ranges from 100 to 450 N/mm². Historically, water pipes were made of cast iron with lamellar graphite (GJL), also known as gray cast iron [4] (Figure 1c). Since the 1950s, however, spheroidal graphite cast iron (GJS), formerly known as globular gray cast iron (GGG) or ductile cast iron, has become more common (Figure 1d). Depending on the wall thickness, GJS has a high tensile strength of 300 to 1,400 N/mm² and an elongation at break of up to 22% at a wall thickness of 30 mm [5,6]. It is also forgeable and weldable. According to EN 1563 [7], the matrix of GJS should predominantly consist of ferrite, with a maximum of 5% pearlite (a mixture of ferrite and cementite), and the mass of free cementite should not exceed 1%. The further chemical composition of cast iron with nodular graphite is:

- Carbon: 3.2 to 3.8%
- Silicon: 2.0 to 2.8%
- Manganese: <0.5%,
- Magnesium or cerium: 0.5%.

Spheroidal graphite cast iron is widely used in industry due to its good mechanical properties, low-cost production, and good machinability. Approximately 30% of the 15 million tons produced per year are used for the production of centrifugally cast pipes with diameters ranging from 60 to 2,400 mm. These pipes are used for transporting water and gas. ISO 10809-1 [8] provides information on cast iron materials for material selection.

Today, only protected ductile iron pipes are used for drinking water distribution. However, there are still many pipelines that are up to 100 years old. Most of these older pipelines are made of cast iron with lamellar graphite, also known as gray cast iron. Cast iron pipes were produced individually from 1877 horizontally and from 1880 to 1930 vertically in sand molds. First-generation cast iron pipes are characterized by a low corrosion rate and good mechanical stability. During the casting process, a thin layer of fused silicon compounds forms on the surface, providing a degree of corrosion protection similar to enamel. These pipes are still in use in supply networks today without any problems. Around 1926, individual production was replaced by mechanized production using the centrifugal casting process with vertically arranged casting carousels, a process still used worldwide today. Initially, to increase durability, the pipes were dipped in hot asphalt. The development of cast iron with spheroidal graphite (GJS) in 1948 was a decisive advancement in terms of plasticity and formability. Because GJS corrodes, **surface protection** was applied:

until 1960: External protection with zinc and a bituminous topcoat,
1966: Dipping in tar on the inside and outside,
1970: Cement mortar lining,
Since 1995 with external protection (zinc, epoxy resin or polyurethane).

However, the protective measures prior to 1970 were not totally successful. For example, in the past, bitumen fragments blasted off the inside of pipes were frequently found in elevated tanks. Today, these fragments are rare. The brief use of tar-impregnated pipes posed a health risk because tar, a coal product, contains high quantities of polycyclic aromatic hydrocarbons (PAHs), which leaked into the drinking water. After PAHs were included in the 1975 German Drinking Water Ordinance, utility companies identified and replaced the affected pipes after intensive investigations, so the problem should no longer exist today. Nevertheless, it is reasonable to assume that all pipes in the network from

before 1970 do not have intact internal protection and corrode to varying degrees depending on the conditions. Cast iron pipes used to transport drinking water must comply with EN 545 [7], which requires internal and external protection. For drinking water application, protection is provided by an **external cement mortar coating or a zinc layer of at least 70 µm** covered by a bitumen or polymer top layer. The **inner coating consists of cement mortar** with a minimum thickness of 4 mm for nominal diameters ranging from 40 to 300 mm. Cement mortar linings have the advantage of a certain "self-healing power," as increased pH values in pores or cracks lead to calcite growth and can seal small defects in the lining when the cement is young. However, joints and cracks should not exceed 4 mm in width, as otherwise they become points of attack for corrosion. The delivery conditions for water intended for human consumption and for non-alloy steel tubes and fittings are found in EN 10224 [9]. The European standard EN 12068 [10] can be consulted for cathodic protection.

2.2. Low-alloy steel in drinking water distribution

According to EN 10020, steel is an iron-carbon alloy that contains less than 1.5% carbon and small proportions of other elements [11]. Carbon steel is further organized into three main categories [12]:

- Low carbon steel (or mild steel) is one of the most common types of carbon steel, with a carbon content between 0.04% and 0.30%. Common grades of mild/low carbon steel include ASTM A36, SAE 1008, and SAE 1018.
- Medium carbon steel has a carbon range of 0.31% to 0.60%, and a manganese content ranging from 0.60% to 1.65%. Common grades of medium carbon steel include the range of AISI/SAE 1030-1055, as well as 4140.
- High carbon steel, also known as tool steel, has a carbon range between 0.61% and 1.50%. Common grades of high carbon steel include the range of AISI/SAE 1060-1095, as well as A2, D2, M2, and H13.

A publication of the German Institute of Standards (DIN) can be used to compare US and European steel grades [13].

Steel can be cast, as well as cold- and hot-formed (i.e., forged, bent, rolled, and drawn). It has high tensile and compressive strength (modulus of elasticity: 2.1×10^5 N/mm²), good rigidity, and an elongation at break of up to 50% [3]. In the drinking water sector, low-alloy steel is used for transport pipes with larger diameters (> 200 mm). Steel pipes have significantly thinner walls than cast iron pipes, and they are weldable. However, unalloyed and low-alloy steels, like cast iron, are not suitable for drinking water pipes without internal protection [7]. Cement, epoxy resin, and nylon 11 (Rilsan®) coatings are mainly used for corrosion protection in distribution networks, while galvanized steel pipes and components are used in drinking water installations.

2.3. Stainless steel

Stainless steel consists of an iron alloy containing 17 to 18% chromium, 12 to 14% nickel, 2 to 3% molybdenum, and a maximum of 1.2% carbon. Drinking water pipes are produced by longitudinal seam welding. To prevent corrosion, the inner and outer surfaces must be smooth and residue-free. Additionally, the weld seams must be smooth and residue-free. Outside diameters of pipes range from 12 to 330 mm. According to the UBA's "Assessment Basis for Metallic Materials in Contact with Drinking Water," stainless steels can be used without restriction in the passive state for all product groups, including pipes, fittings, and components [14]. However, at high chlorine concentrations, localized crevice or pitting corrosion can occur in some stainless steels. Since stainless steels are significantly more expensive due to their alloy components, they are used almost exclusively in drinking water installations.

3. Corrosion of ferrous materials

Depending on the composition and pH value of the water, different corrosion mechanisms and **types of corrosion** can be distinguished for ferrous materials. The corrosion rate of iron is determined by the amount of iron removed per unit area and time. With an iron molar mass of 55.85 g/mol and a density of 7.87 kg/dm³, **corrosion rates for ferrous materials** can be converted as follows [15]:

1 g/m²/d = 0.0464 mm/year = 46.4 µm/year = 1.81 mpy (0.001 in/year).

As the temperature rises, oxygen-dependent corrosion of iron increases by a factor of three up to 70 °C, after which it falls back to the level of attack at room temperature up to the boiling point. The decrease in corrosion at higher temperatures is due to the decreased solubility of oxygen in water. Figure 2a shows the corrosion of iron in water as a function of oxygen concentration with and without carbon dioxide at 60 °C. Without carbon dioxide, removal is linear with respect to oxygen concentration. As can be seen, carbon dioxide also increases the corrosive attack. Figure 2b shows that carbon dioxide alone is corrosive to iron, which can be explained by the presence of carbonic acid.

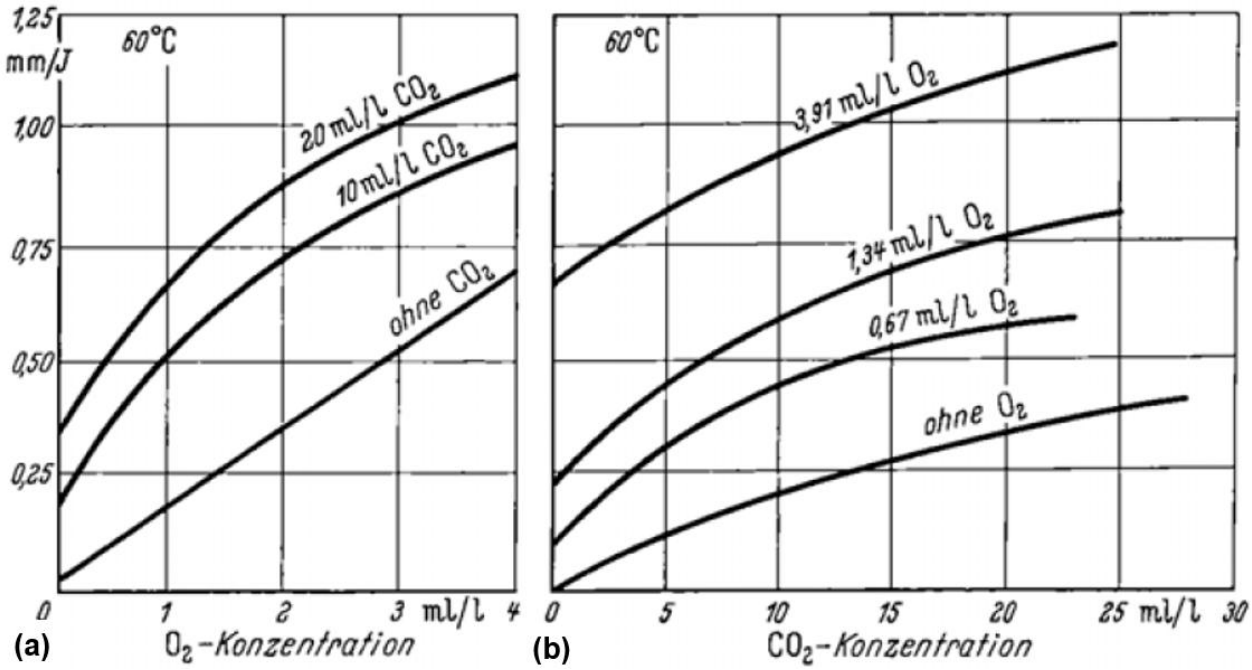


Figure 2: Corrosive erosion of low-alloyed steel (0.15% carbon) in water at 60 °C as a function of **(a)** oxygen concentration and **(b)** carbon dioxide concentration [16].

The strong increase in corrosion rates with temperature is responsible for the increase in corrosion phenomena on cast iron pipes at higher outdoor temperatures. Due to the increase in maximum temperatures resulting from climate change, previously inconspicuous drinking water pipes will become conspicuous, especially in areas with low ground cover.

The corrosion rate of ferrous materials can be reduced by forming stable corrosion-product coatings, called scales, that cover the metal surface. Corrosion tests and standards are published [17].

3.1. Hydrogen ion reduction

Iron is unstable in air-free water and reacts in the first step to form iron(II) hydroxide and hydrogen, as shown by Equation 1. As the concentration of hydrogen ions decreases, the reaction stops at pH 7.5. The formed iron(II) hydroxide is also oxidized in water

(Equation 2), which produces hydrogen. The final product is iron(III) hydroxide oxide [16].

$$Fe + 2\ H_2O \rightarrow Fe(OH)_2 + H_2 \quad (1)$$

$$2\ Fe(OH)_2 + 2\ H_2O \rightarrow 2\ Fe(OH)_3 + H_2 \quad (2)$$

Above pH 9, alkaline corrosion begins with the formation of hydrogen. The hydrogen formed can diffuse into the remaining metal and significantly deteriorate the material properties of the remaining iron.

3.2. Oxygen corrosion

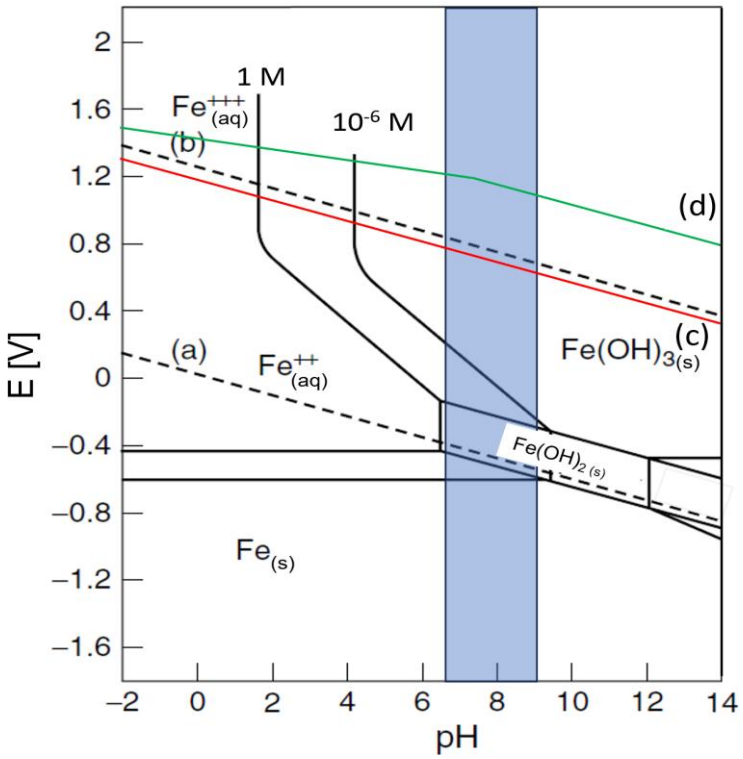
In oxygen corrosion, iron reacts with oxygen according to Equation 3 to form iron(II) hydroxide. If sufficient oxygen is supplied, the iron(II) hydroxide is further oxidized to iron(III) hydroxide according to Equation 4.

$$2\ Fe + O_2 + 2\ H_2O \rightarrow 2\ Fe(OH)_2 \quad (3)$$

$$4\ Fe(OH)_2 + O_2 + 2\ H_2O \rightarrow 4\ Fe(OH)_3 \quad (4)$$

Approximately 3% of total iron corrosion is due to hydrogen ion corrosion, while over 90% is due to oxygen corrosion.

The Pourbaix diagram for iron (Figure 3) shows the thermodynamic stability of the main substances involved in corrosion as a function of pH and redox potential [18]. However, this depends on the species considered. Figure 3 does not take iron hydroxide, oxide, or anhydrous iron oxides into account, for example. The indices "(s)" and "(aq)" stand for solid and substance dissolved in water (Latin: aqua), respectively.



(a) **(b)**

Figure 3. Pourbaix diagram for the iron-water system at 25 °C with two concentrations of dissolved iron: 1 M and 10^{-6} M. The dashed lines illustrate the cathode reactions of water: **(a)** oxygen formation, **(b)** hydrogen formation, **(c)** redox potentials of 2 mg/L dissolved oxygen, **(d)** redox potentials of 2 mg/L free chlorine. Modified according to [18].

For iron corrosion in drinking water, the important pH range is ≥ 6.5 and ≤ 9.5 (the blue area), as corrosion begins at an iron concentration of 10^{-6} M (0.0558 mg/L), when there are no dissolved iron species or corrosion products present.

Figure 3 shows that iron is not stable in water unless a potential of less than -0.6 volts is applied. As the potential increases, **iron(II) hydroxide** forms with a narrow stability range. Further increases in potential result in iron(III) hydroxide becoming the more stable species. During water splitting, **amorphous iron(III) hydroxide** transforms into the crystallized **minerals lepidocrocite or goethite**. This phase transformation is not shown in the Pourbaix diagram (Figure 3). **Magnetite** (iron(II/III) oxide), **hematite** (iron(III) oxide), and **siderite** (iron(II) carbonate) are also found in older, thicker layers of rust. Whether a stable top layer of iron oxides and hydroxides forms, protecting the material from further corrosion, depends on the medium and operating conditions.

Because each drinking water has a unique composition, each water will have different corrosion properties with the same materials and operating conditions. **Oxygen** is the most important oxidizing agent in drinking water. The addition of **disinfectants**, such as chlorine or chlorine dioxide, also promotes corrosion because they are oxidants. While today's drinking water is almost always oxic, i.e. has an oxygen content above 3 mg/l, while raw water can be anoxic ($c(O_2) \leq 3$ mg/l). In the absence of oxygen, other species occur as oxidants, such as nitrate or sulfate, and nitrite, ammonium, or hydrogen sulfide may be formed as reduction products. Today, oxygen concentrations of > 3.2 mg/l (> 0.1 mmol/L) are used in drinking water to achieve the formation of a stable corrosion layer for unprotected iron materials.

Steel has a significantly lower carbon content and a more positive electrode potential than cast iron, resulting in a lower corrosion rate. However, the addition of nobler metals, such as copper, greatly increases the rate of hydrogen corrosion of iron. Conversely, the addition of other alloy components, such as silicon, strongly reduces corrosion as the content increases [15].

3.3. Instationary corrosion

The unpleasant phenomenon of "rust water" or "brown water" occurs when brown, cloudy, particle-laden water emerges from cast iron and unalloyed steel pipes after several hours of stagnation. This results in complaints from consumers and restrictions on the product's usability for private and commercial purposes. However, after flushing the pipes and ensuring regular water withdrawal, the symptoms usually cease. The cause was identified as **lepidocrocite** (γ-iron(III) hydroxide oxide), which, unlike goethite (α-iron(III) hydroxide oxide), is redox-active and maintains the corrosion process even after oxygen is depleted (Equation 5). This process forms and releases iron(II) into the water and is referred to in Germany as "instationary corrosion" [19].

$$Fe + 2\ FeOOH + 2\ H^+ \rightarrow 3\ Fe^{2+} + 4\ OH^- \quad (5)$$

If iron(II)-containing water comes into contact with oxygen-containing water, as occurs during transport, the iron(II) is rapidly oxidized to trivalent iron. The iron(III) then hydrolyzes and forms the sparingly soluble iron(III) hydroxide, which is dispersed in the water and known as "rust water." **Possible countermeasures include preventing stagnation, increasing the oxygen concentration, and adding inhibitors** that promote the formation of goethite over lepidocrocite [20].

Corrosion processes in water pipes and incomplete removal of dissolved iron and manganese from raw water during treatment can lead to brown discoloration of drinking water. Even if limit values for drinking water are met at the waterworks outlet, residual concentrations of iron and manganese form particles that settle in certain areas, but are mobilized by higher flow velocities. These sediment deposits can be colonized by microorganisms, which can lead to contamination. Therefore, it is good practice to regularly remove them from the network through systematic pipe flushing.

4. Types of attack on cast iron and unalloyed and low-alloy steel

Depending on the alloy composition, microstructure, surface condition, water, and operating conditions (flow velocity and temperature), cast iron and steels (unalloyed and low-alloy) can exhibit different types of corrosive attack. According to EN 12502-1 [21], a distinction is made between nine types of corrosion. Of these, the following are important for cast iron, unalloyed steels, and low-alloy steels, according to EN 12502-5 [22]:

- **uniform surface corrosion;**
- **pitting corrosion;**
- **selective corrosion;**
- **bimetallic corrosion;**
- and **erosion corrosion.**

Uniform corrosion, which affects the entire surface of the material, is the most common type of corrosion. The corrosion process is diffusion-controlled, and the rate depends on the pH value (hydrogen ion corrosion) or the oxygen concentration (oxygen corrosion). Surface corrosion rarely leads to corrosion damage.

A **protective layer** is likely to form if the water fulfills the following parameters:

- **oxygen concentration > 2.8 mg/L (> 0.1 mmol/L);**
- **pH value > 7.0;**
- **bicarbonate concentration > 122 mg/L (> 2 mmol/L);**
- **calcium ion concentration of > 44 mg/L (> 1 mmol/L).**

Instationary corrosion (see section 3.3) may occur if surface corrosion is present and the water periodically stagnates.

Even if a protective layer does not form, surface corrosion can be avoided by maintaining a high pH (> 8.5) and ensuring the water is oxygen-free (< 0.084 mg/L). However, these conditions are rarely found in drinking water, but are more common in heating or district heating systems. The advantage is that the increase in corrosion rate with temperature is not significant because the low oxygen concentration limits material removal. District heating water, which reaches temperatures of 110 to 130 °C in winter, undergoes additional alkalization to suppress hydrogen corrosion.

4.2. Pitting corrosion

Pitting corrosion involves highly localized metal removal, resulting in the rapid formation of pinholes. This type of corrosion is the most common cause of damage to unalloyed and low-alloy steels, as well as cast iron, in water distribution and storage systems. Pitting corrosion is caused by areas with different oxygen concentrations. On the water side, the probability of pitting corrosion decreases with increasing bicarbonate concentration and increases with increasing chloride, nitrate, and sulfate concentrations [22].

4.3. Selective corrosion of cast iron

In cast iron with lamellar or spheroidal graphite, **selective corrosion primarily affects the iron portion of the material and mainly occurs in older pipes**. The graphite phase, on the other hand, is inert but promotes the formation of localized elements. The dissolution rate increases continuously with increasing carbon content, reaching a rate around a hundred times higher with 1% carbon than with pure iron [15]. Without a dense protective layer, the iron is anodically dissolved from the wall and carried away. What remains is graphite as a cathode and a phosphate eutectic. While the shape is retained, the strength is lost. The affected pipe retains its shape, but it loses stability, and large areas of the pipe wall flake off in a process known as "shell fractures." This type of corrosion is known as **spongiosis** or **graphitization**.

4.4. Bimetallic or contact corrosion

This type of corrosion occurs when precious and non-precious metals are installed in the same piping system, creating mechanical and metallic connections between them, as

well as contact with the same electrolyte. This results in a redox reaction, in which the base metal dissolves and deposits on the noble metal. This causes pitting corrosion at the joint. This type of corrosion often occurs in practice when iron or low-alloy steel is used with stainless steel, copper, or copper alloys, such as bronze, brass, or gunmetal. A common countermeasure is to galvanically separate the components to stop the reaction.

4.5 Erosion corrosion

This type of corrosion involves the removal of material due to corrosion and **mechanical surface removal (erosion) caused by high flow velocity**. The corrosion is triggered by the destruction of protective layers caused by erosion. Bare metal and depressions in the material often appear at the affected points, widening in the direction of flow and leading to pitting corrosion damage in the long term.

5. Types of attack on stainless steel

Although stainless steels are not completely immune to corrosion, they are passivated by the formation of a very thin, hard top layer of chromium oxide. Nevertheless, corrosion damage can occur with low probability depending on the boundary conditions. According to EN 12502-4 [23], the following must be observed:

- **pitting corrosion,**
- **crevice corrosion,**
- **stress corrosion,**
- **knife-edge corrosion,**
- and **corrosion fatigue.**

Only pitting and crevice corrosion are discussed here.

5.1 Pitting corrosion

This only occurs when a more positive potential than that of the stainless steel is present. One reason may be if the surface is partly contaminated by grease or deposited particles, which create local elements. Improper welding processes that alter the material's structure are also a known cause. The probability of pitting corrosion increases with high chloride ion concentrations in water. In cold water, the probability increases at 210 mg/L of chloride, a concentration that rarely occurs in drinking water. In hot water, the probability of corrosion increases at 53 mg/L of chloride.

5.2 Crevice corrosion

Crevice corrosion can occur when stainless steel is joined to a non-conductive material and a gap of less than 0.5 mm remains between them. This is caused by minor leaks or sealing materials with low chloride content, which lead to corrosion of the joint.

The next article deals with simple methods for determining the corrosion rate of unalloyed steel and instationary corrosion.

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