Educational Article

Corrosion Control in Drinking Water Distribution Using Simple Methods

Part 2: Water and the Influence on Corrosion

Norbert Konradt, Monika Konradt und Peter Janknecht, Trinkwasser Consulting, 45355 Essen, Germany

Contact: info@trinkwasser-consulting.de

Summary: Water is a simple chemical compound with many unusual properties that also make it a corrosive medium in metallic pipelines. Oxygen and carbon dioxide are dissolved through contact with the environment. The oxygen corrodes the metals and the carbon dioxide with its acidic properties promotes corrosion. Due to the high polarity of the water, many salts and polar organic substances can also be dissolved, which intervene in the corrosion processes in different ways.

Keywords: Electrical conductivity, chlorine-hypochlorite equilibrium, lime-carbonic acid equilibrium, pH value, polarity of water, redox potential, Pourbaix diagram, solubility.

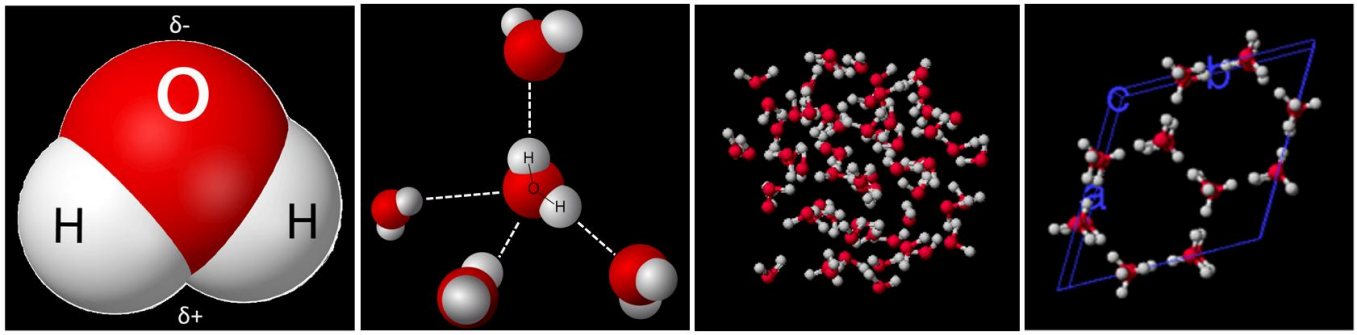
Foreword: What is the purpose of this series of articles?

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. Physical and thermodynamic properties of water

Water is a compound made up of the elements hydrogen and oxygen. The best-known process for the formation of water is the combustion of hydrogen with oxygen in an oxyhydrogen flame or the electrochemical reaction in a fuel cell. The smallest unit is a water molecule: H_2O. Due to the different electronegativity of its elements, water molecules are electric dipoles, with a positive partial charge on the hydrogen side and a negative one on the oxygen side (Figure 1a).

From a macroscopic point of view, water is a **strongly polar compound**. The dipoles lead to the formation of **hydrogen bonds**, whereby a water molecule can be connected to up to four others, two via the hydrogen atoms and two via the two free electron pairs of the oxygen (Figure 1b). When further water molecules are attached, water clusters are formed which are not stable over time, but fluctuate by breaking and forming new hydrogen bonds with other water molecules (Figure 1c). The water clusters are for instance responsible for the high boiling point of water.



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

Figure 1 (a) The water molecule with partial charges on oxygen (δ-) and hydrogen (δ+), **(b)** Hydrogen bonds to a maximum of four other water molecules, **(c)** Water molecules and clusters in liquid water, **(d)** Ice crystal. (https://www.chamotlabs.com/Molecules/Water.html).

The high polarity of water (dielectric constant of 80.35 at 20 °C) results in good **solubility of salts, polar organic substances (proteins, sugars)** and moderate solubility for **gases**. **Salts, acids and bases largely decompose in water to form ions**, which are surrounded (hydrated) by water molecules. With a few exceptions, the solubility of salts in g/100 g water increases with temperature, although the increase varies greatly. For substances with very low solubility, the solubility product (L_P) is used, which obtained by multiplying the ion concentrations involved, e.g. $L_P(Ca(OH)_2) = [Ca^{2+}]*[OH^-]^2$. Table 1 gives an overview of the solubilities and solubility products in pure water.

Table 1: Solubilities and solubility products of solids in water [1].

	Solubility [g/100 g water]	**Solubility product** [1]	**Temperature [°C]**
Calcium carbonate	-	$8.7 * 10^{-7}$	
Calcium chloride	73.,9		25
Calcium hydroxide	-	$4.3 * 10^{-2}$	18
Calcium sulfate * 2 H_2O (gypsum)	0.25	$6.1 * 10^{-5}$	25
Copper(I) chloride (cuprous chloride)		$1 * 10^{-6}$	18
Copper(II) hydroxide		$5.6 * 10^{-20}$	18-20
Copper sulphate	21.4		
Iron(II) hydroxide		$4.2 * 10^{-16}$	18
Iron(III) hydroxide		$3.8 * 10^{-38}$	18
α-Iron oxide hydroxide		$1.0 * 10^{-42}$	-
γ-Iron oxide hydroxide		$1.0 * 10^{-40}$	-
Iron(II) sulfate	26.5		
Sodium chloride	36.0		
Sodium hypochlorite * 5 H_2O	325.6		
Sodium hydroxide	108.3		

[1] The unit of the solubility product results from the product of the units of the ions involved, usually in mol/L, exponentiated with the stoichiometric factors.

The solubilities of **calcium carbonate**, **calcium sulfate dihydrate (gypsum)**, and **iron(III) oxide-hydroxide (ferric oxyhydroxide)** are almost never exceeded in drinking water. However, they are of technical significance, e.g., the formation of deposits.

At higher temperatures, solid calcium carbonate is formed from dissolved calcium hydrogen carbonate (Equation 1). These deposits, known as scale, often form on heat exchangers and in boilers, reducing heat transfer. For this reason, Germany maintains a list of approved treatment substances and disinfection processes, including scale inhibitors, which are added to drinking water within a specific concentration range [5]. Scale formation is important in steam generation from drinking water because the salts become concentrated.

$$Ca^{2+} + 2\ HCO_3^- \leftrightarrows CaCO_{3(s)} + CO_2 + H_2O \quad (1)$$

(s): solid

The total amount of dissolved and dissociated salts is measured using electrical conductivity as a sum parameter. This is defined as the reciprocal of the electrical resistance and is usually specified for drinking water in the unit µS/cm [3]. According to the **EU Drinking Water Ordinance** [4], the maximum allowable electrical conductivity value is 2500 µS/cm, measured at 20 °C [4], since drinking water should not be corrosive.

In contrast, according to Henry's law, gases dissolve in water in proportion to their partial pressure (i.e., the pressure of the gas above the liquid). The solubility of oxygen in water when it comes into contact with air is lower than what is indicated in Table 2, depending on the proportion of oxygen in the air. For instance, 14.6 mg/L of oxygen dissolves at 0.1°C [3]. Unlike solids, the solubility of gases decreases with increasing temperature, reaching only 9.08 mg/L for oxygen at 20 °C. In addition to physical dissolution, gases can react with water. For example, carbon dioxide and chlorine react with water.

Table 2: Solubilities of gases in water [2].

Substance	Solubility [mg/l]	Temperature [°C]
Chlorine	7280	-
Oxygen	43	0
Ozone	570	-
Nitrogen	23	0
Carbon dioxide	1690	20

In addition, water has many unusual properties, or **anomalies**, of which more than 50 are known to date. These anomalies have important implications for technology, chemistry, and biology. For instance, water exists on Earth in **three states: ice, liquid water, and steam**. Pure water freezes below 0°C and boils at 100°C. These values are both very high compared to those of chemically similar compounds, such as ammonia or hydrogen sulfide. When dissolved substances are present, the freezing point usually decreases (the water freezes below 0 °C), and the boiling point usually increases (the water boils above 100 °C). With a **high specific heat capacity** of 4.19 kJ/(kg*K), water can absorb twice the amount of heat required to heat ethanol by one degree. However, water's specific heat capacity has a minimum at 35 °C. Therefore, it is energetically expensive to heat water; however, water also stores thermal energy well. Additionally, water has a **high enthalpy of vaporization** of 2,453 kJ/kg at 20 °C, which results in a cooling effect during transpiration. The **density anomaly** is particularly important: water has its greatest density at 4°C. Ice has a lower density than liquid water and floats because the arrangement of water molecules in its crystalline state takes up more space (Figure 1d). Consequently, lakes and rivers freeze from the top down at temperatures below 0 °C, creating an environment for aquatic plants and animals beneath the ice. Almost all other liquids behave in the opposite way. Water's **surface tension** is also higher than that of comparable liquids. Water's **high light transmission** in the visible range of the

electromagnetic spectrum enables algae and plants to live in it because they need light. UV light is only significantly absorbed by water below 240 nm. This allows water to be disinfected as part of the drinking water treatment process.

2. Chemical properties of water

In addition to the physical and thermodynamic characteristics mentioned above, water has other chemical properties. Highly pure, salt- and gas-free water has low conductivity, which is due to **self-dissociation**. A small percentage of water molecules decompose into hydrogen ions (H^+) and hydroxide ions (OH^-), with a concentration of 10^{-7} mol/L each in pure water. These two species are surrounded by H_2O molecules and coexist in water separately. (Equation 2).

$$H_2O \leftrightarrows H^+ + OH^- \qquad (2)$$

The acidic or alkaline character of water is indicated by the **pH value**, which is defined as the negative decadic logarithm of the hydrogen ion concentration (Equation 3) and has a value of 7 in neutral water (at 22 °C). pH values below 7 indicate an acidic character, higher values indicate an alkaline character. Deviations from the ideal behavior can be made by introducing the ion activity instead of concentration (a = f * c), but this is not relevant for standard applications. Since drinking water should not be aggressive, the **EU Drinking Water Ordinance requires a pH value between 6.5 and 9.5.** [4].

$$pH = -\log c(H^+) \qquad (3)$$

Pure water has no buffering effect, i.e. it reacts to even small additions of acids or bases with large changes in pH value. When a strong acid is added, it dissociates completely and increases the concentration of hydrogen ions, which lowers the pH value. For example, dissolving 0.1 mol (3.6 g) of HCl gas in one liter of water leads to complete dissociation and a pH of 1.0. Water acts as a base in the process and supports the dissociation (Equation 4). Compared to stronger bases such as ammonia, however, water behaves as an acid (Equation 5). This behavior is referred to as **amphoteric behavior**.

$$\text{as base: } HCl + H_2O \leftrightarrows H_3O^+ + Cl^- \qquad (4)$$

$$\text{as acid: } NH_3 + H_2O \leftrightarrows NH_4^+ + OH^- \qquad (5)$$

3. The lime-carbonic acid balance

When carbon dioxide is introduced into pure water, it undergoes physical dissolution and additionally reacts—via the uptake of water—to form carbonic acid (Equation 6), which subsequently dissociates into ions in accordance with Equation 7 [6]. The concentration of carbonic acid is low, and the equilibrium lies predominantly on the left side of the equation. The water tastes acidic. The pK_a values are the negative logarithms of the acid dissociation constants; the more strongly an acid dissociates, the lower its pK_a value.

$$CO_2 + H_2O \leftrightarrows H_2CO_3 \qquad pK_S = 6.35 \quad (6)$$

$$H_2CO_3 + H_2O \leftrightarrows H_3O^+ + HCO_3^- \qquad pK_S = 10.33 \quad (7)$$

Hydrogen carbonate (also known as bicarbonate) can react as an acid under alkaline conditions, release a proton and form carbonate (Equation 8).

$$HCO_3^- + OH^- \leftrightarrows CO_3^{2-} + H_2O \qquad (8)$$

At low pH values, carbon dioxide and traces of carbonic acid are predominant in the water, between pH 7 and 9 the hydrogen carbonate ions dominate, and at high pH values

the carbonate ions dominate. The concentration ratios of the species involved as a function of the pH value can be shown in an existence diagram (Figure 2).

In the pH range of 4.5 to 7.8, where drinking water is mostly found, bicarbonate and carbon dioxide are the relevant species, while carbonate can be neglected up to a pH of 9.5. The **base capacity** can be measured by titrating with 0.1 mmol/L sodium hydroxide to a pH of 8.2. This value is equal to the amount of free **carbon dioxide**. The **acid capacity** is determined by titrating with 0.1 mmol/L hydrochloric acid to a pH of 4.3 and results in the **bicarbonate concentration**. Both parameters are important for assessing carbon dioxide equilibrium data, for which there are standards in Germany [7].

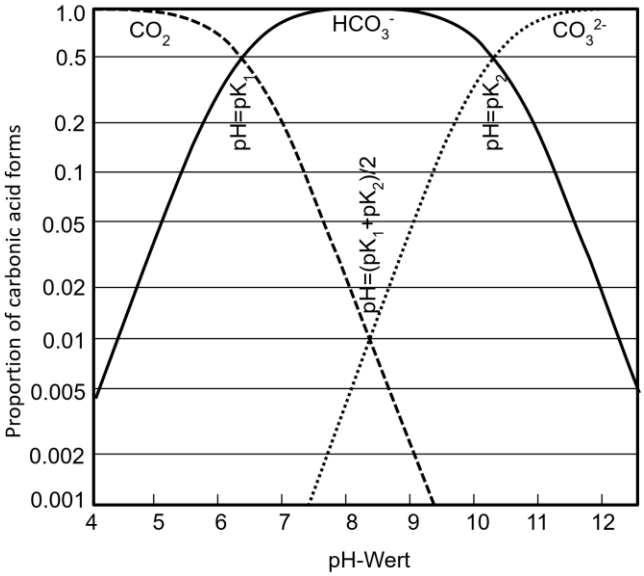


Figure 2: Existence ranges of CO_2 , HCO_3^- and CO_3^{2-} in water as a function of pH (taken from Johannes Kalliauer, modified - http://www.trinkwasserspezi.de/Image3.gif, CC BY-SA 4.0, https://commons.wikimedia.org/w/index.php?curid=86170265).

Natural waters containing bicarbonate have a **buffering capacity** between pH 6.5 and 8, i.e. the pH value increases less when acid or base is added than in pure water. In this way, pH fluctuations, e.g., in blood are buffered.

Acidic water is corrosive to many materials, such as cement and metals. When carbonated water comes into contact with calcium carbonate, the calcium carbonate dissolves until equilibrium is reached, according to Equation 1.

4. The chlorine-hypochlorite equilibrium

When chlorine gas (Cl_2) is introduced into water, it dissolves and partially decomposes into hydrochloric acid and hypochlorous acid (Equation 9).

$$Cl_2 + 3\ H_2O \leftrightarrows 2\ H_3O^+ + Cl^- + ClO^- \qquad (9)$$

The process is called **disproportionation** because two chlorine compounds are formed from elemental chlorine with an oxidation state of zero, one in a higher oxidation state (hypochlorite, +1) and one in a lower oxidation state (chloride, -1). While the hydrochloric acid in drinking water forms chloride, which is a natural component of many drinking waters and only rarely changes its oxidation state through redox processes, the hypochlorous acid is a weak, less dissociated acid and a strong oxidizing and disinfecting agent that even outperforms chlorine with an oxidation potential of E° = 1.35 V (Equation 10). Dosing is therefore particularly effective at pH values of 7 and below.

$$HOCl + 2\ e^- \leftrightarrows Cl^- + OH^- \qquad (10)$$

E° at pH = 0: +1.495 V, at pH = 14: +0.855 V

As chlorine is a dangerous gas from a safety point of view and tends to be used for continuous dosing, many waterworks use a sodium hypochlorite solution for temporary dosing. This solution is produced by adding chlorine to caustic soda, is highly alkaline and creates an equilibrium of hypochlorite and hypochlorous acid in the drinking water. According to the German list of permitted treatment substances, a maximum dose of 1.2 mg/L of chlorine or 1.5 mg/L of hypochlorite is allowed [5]. As strong oxidizing agents, chlorine and hypochlorous acid influence the corrosion process of metal supply lines, in addition to their disinfecting properties.

4. Redox potential and redox voltage

Naturally occurring oxygen and the technically produced substances chlorine and hypochlorite occur as oxidizing agents in drinking water. Ozone and potassium permanganate are also used in water treatment, but these are broken down relatively quickly in the water. If several oxidizing agents are present in the water, the highest redox potential dominates. A measure of the redox potential of water can be obtained by measuring it against a reference electrode. If a non-indifferent electrode (e.g. made of platinum or gold) is immersed in water with a redox system, e.g. O_2/OH-, a potential is established that can be described using the **Nernst equation** (Equation 11).

$$E_{\text{Redox}} = E° + \frac{R*T}{n*F} * ln\ \frac{c(Ox)}{c(Red)}\ ;\ \text{Unit: V} \quad (11)$$

E°: redox potential under standard conditions, R: general gas constant, T: absolute temperature, n: number of electrons exchanged, F: Faraday constant: Number of electrons exchanged, F: Faraday constant

The half-cell potential is essentially determined by the ratio of the concentrations of the oxidized and reduced redox partners. It increases with increasing concentration of the oxidized form and decreases correspondingly with increasing concentration of the reduced form. If the ratio c(Ox)/c(Red) has the value 1, i.e. if both concentrations are equal, the logarithm is zero and the redox potential is then equal to the standard potential (see first article). The potential of a half-cell cannot be measured directly. A redox potential can be measured by combining two half cells. To determine this, the measuring electrode is connected to a reference electrode of known potential (e.g. silver-silver chloride electrode) to form a measuring chain and the resulting voltage (U_G) is measured. As there are different reference electrodes, the measured redox voltage is referred to the standard hydrogen electrode (SHE) for easy comparison. To do this, the known voltage of the reference electrode (U_B) is added to the measured voltage (U_G) against the SWE (Equation 12).

$$U_H = U_G + U_B \qquad \text{Unit: mV} \qquad (12)$$

5. The redox behavior of water and the Pourbaix diagram

Water itself is redox-active and can be oxidized and reduced. It oxidizes many metals (e.g. iron, zinc) to form hydrogen, whereby the oxidation number of the hydrogen is reduced from +1 in the water molecule to zero in the elemental hydrogen (Equation 13).

$$Zn + 2\ H_2O \rightarrow Zn^{2+} + 2\ OH^- + H_2 \qquad (13)$$

The oxidic oxygen of the water with the oxidation number -2 to zero in the oxygen is oxidized during the electrolysis of water at the anode. At the same time, hydrogen ions are discharged at the cathode (Equation 14).

$$2\ H_2O \rightarrow 2\ H_2 + O_2 \qquad (14)$$

At a pH value of zero, electrolysis should take place at > 1.3 V, in an alkaline solution at pH 14 from > 0.4 V. Due to excess voltages at the electrodes and cell resistances to be overcome, the actual voltages are significantly higher, e.g., in an alkaline solution at approx. 1.9 V. The stability ranges of the individual species can be represented in a **Pourbaix diagram**, which is also used to describe the corrosion processes of metals in contact with water (Figure 3). The applied potential is plotted as a function of the pH value [8].

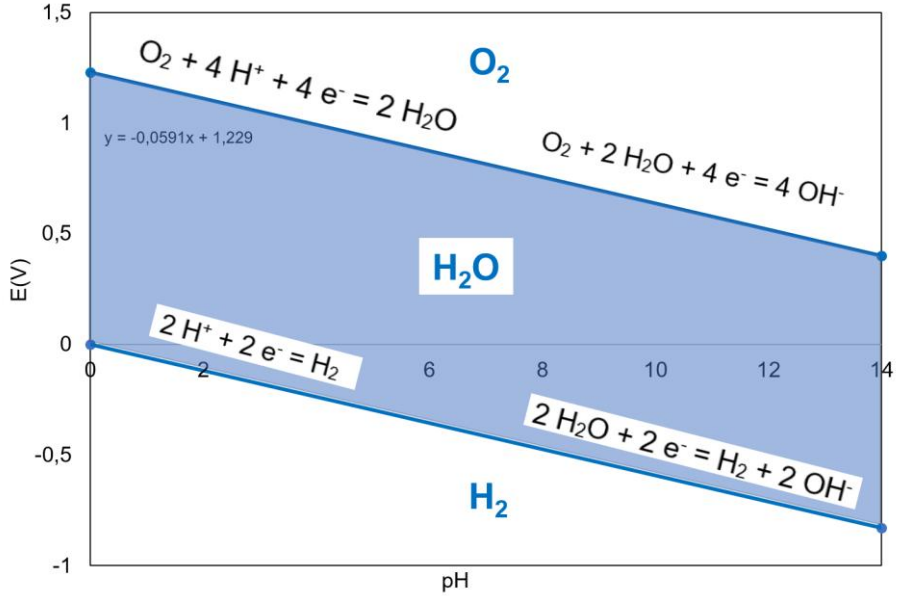


Figure 3: Pourbaix diagram for water, including stability ranges for water, oxygen and hydrogen at standard temperature and standard pressure.

The Pourbaix diagram shows the stability ranges for hydrogen, water (highlighted in blue) and oxygen in equilibrium. Water at pH = 0 is stable from 0 V to 1.3 V. At potentials lower than zero, hydrogen is formed reductively; at potentials higher than 1.229 V, oxygen is formed oxidatively. Excess voltage often occurs at real electrodes with current transport, so that the potentials increase. Inclined lines in the Pourbaix diagram indicate electrode reactions with the participation of protons or hydroxide ions, which means that the process is dependent on the pH value.

The next article deals with the properties and corrosion of cast iron and steel.

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