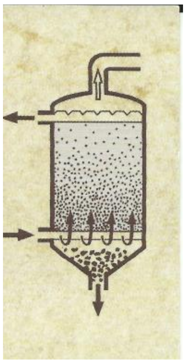
Prof. Dr. Peter M. Kunz
BIO-LOGIK-CONTROL

Am Oberen Luisenpark 2
D-68165 Mannheim
☎: 0621/318804-70
🖷: 0621/318804-71
✉: peter.m.kunz@t-online.de

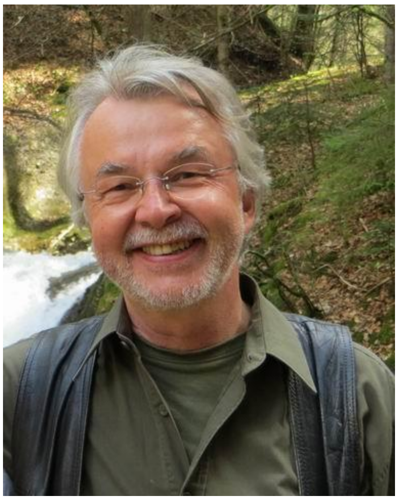


BIO-LOGIK-CONTROL ♦
Am Oberen Luisenpark 2♦ D-68165 Mannheim

03.07.2018

An Herrn Geschäftsführer Marc Flettner
ION Deutschland GmbH
Gesellschaft für Umwelttechnik
Hirschburgweg 5
40629 Düsseldorf

Zinc in water - a metal with interesting effects for Calcium Carbonate - precipitation



Peter M. Kunz

Prof. Dr. Peter M. Kunz

Itemization

- Starting situation
- Zinc – the metal in galvanized water pipes and elsewhere
- Calcium carbonate – forms in water, especially if water is heated (Aragonite formation versus hard lime deposits)
- Corrosion of metals, especially of zinc and along the electro-chemical series
- Water circulation systems – scaling processes
- The principle of AQUABION®
- Test results of zinc separation during AQUABION®
- Balancing thoughts (weight reduction of AQUABION®)
- Health aspects of zinc in water, if it is consumed – (WHO and Drinking Water Ordinance)
- Summarizing core statements – Prospects

1 Starting situation

The company ION Deutschland GmbH runs a zinc sacrificial anode system (AQUABION®) for galvanic water treatment against corrosion and lime deposits. Prof. Kenneth M. Persson of the Technical University of Lund (https://www.lunduniversity.lu.se/lucat/user/73fa053aff3d26a31e6e4ae893da9d9e) reacted publicly to the contents of the Swedish website www.aquabion.se with estimates on the subject of galvanized water treatment with zinc, which has inspired a scientific discussion.

2 Zinc the metal in galvanized water pipes and also elsewhere

On www.chemie.de one reads that “zinc is a chemical element having the symbol “Zn” and atomic number “30“. Zinc is counted among the transition metals, but has a special position there, because due to the closed d-shell, its properties are similar to the properties of alkali metals. It is a bluish-white brittle metal and is, among other things, used in galvanization of iron and steel parts as well as rain gutters.”

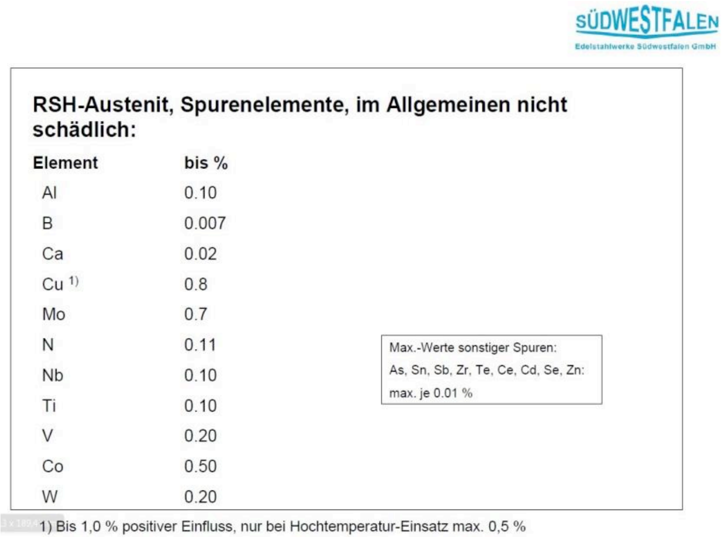
The zinc content in soil according to (www.initiative-zinc.de/) is between 10 and 300 mg/kg. In mineral deposits, zinc is enriched through natural geological and geo-chemical processes by 5 to 15 % (50,000 to 150,000 mg/kg). The ore contains zinc mostly as Sphalerite or Wurtzite, it is also called zinc blende (ZnS). Zinc ore, which is enriched by 55 % of zinc, contains in concentrate form approx. 20 % sulfur. Moreover, zinc concentrate always has iron, lead and silver in different proportions, because these elements occur jointly in the ore (www.initiative- zinc.de/basiswissen/das-metall-zinc/zincerzeugung/). In addition, appreciable quantities of Cadmium also occur, because zinc and cadmium are found together [Kunz, P.M., E. Böhm, U. Hauser: Report on cadmium hearing Berlin (Nov. 1991)].

Taken from WIKIPEDIA [https://de.wikipedia.org/wiki/Zinc]: “Another zinc ore is calamine which is denoted as Smithsonite (also *Zinc spar*) $ZnCO_3$ (approx. 52 % zinc) as well as Willemite $Zn_2[SiO_4]$. Moreover, there are rare zinc minerals like, among other things, zincite (also red zinc ore) ZnO (approx. 73 % zinc), Hemimorphite $Zn_4(OH)_2[Si_2O_7]$ (54 % zinc), Adamine $Zn_2(AsO_4)(OH)$ (approx. 45 % zinc), Minrecordite $CaZn[CO_3]_2$ (approx. 29 % zinc) and Franklinite (Zn,Fe,Mn) $(Fe_2Mn_2)O_4$ (16 % zinc). On the whole (status as in 2010) about 300 zinc minerals are known.”

Pipes made of galvanized steel are being used in sanitary and heating technology for several years; today they are to be found wherever water is not heated or is not heated above 60 °C, e.g., in air-conditioning technology. Depending on the composition of the minerals in water, there is formation of an oxide layer on the zinc surface with oxygen, which protects the pipe material against corrosion. The effectiveness and maintainability of the zinc coat depends essentially on the manufacturing process and the water quality, but also on contact with other metals (keyword “Electrolysis”, http://www.meisingeringenieurleistungen.de/trinkwasserinstallation-rohrleitungsmaterialien-im-vergleich/). If the water becomes hot, this oxide layer becomes chemically unstable, so that first the zinc layer and then the steel starts to corrode.

Especially in watery systems, all metals are subject to corrosion. You will thus find traces of all elements in water, which are included in the alloys of raw pipes, fittings and other metallic bodies. The regulations of WHO and in Europa provide limit values and benchmark values which are covered in Chapter 9: For zinc, WHO specifies a benchmark value acceptable to consumers of 3 mg/L; in Europa the value fluctuated between 0.1 (EU) and 5 mg/L (Drinking Water Ordinance) since 1972: 1990 saw the Drinking Water Ordinance stipulate a benchmark value of 5 mg/L after a 12-hour stagnation after 2 years and up to 2 years after the installation. Currently, all research indicates that EU has not specified any limit values or benchmark values for zinc in drinking water.

The elution of metals from metal surfaces due to corrosion (electro-chemical metal release) is known at least to all experts; hence no one is surprised that trace elements are eluted from “rust-proof stainless steels like V4A steel “WNo. 1.4401 (X5CrNiMo17-12-2), AISI 316“, which is listed in the DVGW worksheet W541: Basis of the requirements of pipes from non-rusting steels for drinking water house installation (besides 1.4404, 1.4521 and 1.4571), are listed in Graphhics 2.1. This stainless steel is also used frequently in water boilers as heating surface.



RSH-Austenit, Spurenelemente, im Allgemeinen nicht schädlich:

Element	bis %
Al	0.10
B	0.007
Ca	0.02
Cu [1]	0.8
Mo	0.7
N	0.11
Nb	0.10
Ti	0.10
V	0.20
Co	0.50
W	0.20

Max.-Werte sonstiger Spuren:
As, Sn, Sb, Zr, Te, Ce, Cd, Se, Zn:
max. je 0.01 %

1) Bis 1,0 % positiver Einfluss, nur bei Hochtemperatur-Einsatz max. 0,5 %

Graphics 2.1 Trace elements in austenite stainless steel (Ingrid Hofmann, Deutsche Edelstahlwerke Specialty Steel GmbH & Co. KG www.dew-stahl.com

3 **Calcium carbonate** – forms in water, especially if water is heated (Aragonite formation versus hard line deposits)

Calcium carbonate (CAS No 471-34-1) is found in nature, predominantly in three forms:

- As Calcite (lime calcite, double calcite, chalk) → trigonal,
- as Aragonite (in coccolith: shells of algae, fossil in chalk) → ortho-rhombic
- as Vaterite → hexagonal

It is an element in sedimentary limestone, metamorphous marble, stalactite, calcareous slate, chalk formations as well as the sediment slice Oolith and Stromatolith. In lively nature, calcium carbonate exists among other things, in the outer skeleton of crabs, corals, clams and snalis. Other modifications are

- Monohydro calcite (monohydrate of calcium carbonate) and
- Ikait (hexahydrate of calcium carbonate)

Calcite

Calcite (calcite, lime calcite, double calcite) is a very frequently occurring mineral from the mineral class of carbonate and nitrate, $CaCO_3$ – chemical. The molar mass is 100.087 g/mol, the water solubility of calcite is specified as 0.00066 g/100 g H_2O at 20 °C. [http:// www.seilnacht.com/Chemie/ch_caco3.htm (08.06.2018)]

Calcite crystallizes trigonally and develops different crystalline or aggregate shapes. In the pure form. calcite is colourless and transparent. Through multiple refraction due to lattice defects or polycrystalline formation, it can look white, wherein the transparency decreases, and the crystal can assume a yellow, pink, blue, green, brown or black tint due to external additions (see Table 3-1).

Igneous origin, sedimentary and metamorphous; as crystals in the crevices of nearly all stones; as passage in sources (calc sinter terraces); in caves (stalagmites and stalactites). [http://www. seilnacht.com/Minerale/calcarag.htm (08.06.2018)]. Calcite can occur as solid (slice) as well as grainy, as fibrous or in crystals, and it shows in the crystal structure the highest richness in shape among all minerals. Limestone is a sediment stone. It occurs alone or in combination with other minerals. Calcite originated/originates frequently through bio-mineralization. The shells of sea urchins are built from calcite crystals. By far the biggest calcite occurrence dates back to ocean bed deposits. Even coral reefs consist of calcite partially. [www.seilnacht. com/Minerale/calcarag.htm (08.06.2018)]

Discussion on lime – carbonic acid equilibrium and water hardness

In carbonic acid-containing water, the calcium carbonate changes to water soluble calcium hydrogen carbonate

$$CaCO_3 + H_2O + CO_2 \rightleftharpoons Ca^{2+} + 2\,HCO_3^- \text{ (carbonate equilibrium)}$$

The calcium ions arising therefrom constitute a big part of the water hardness in watery solutions.

The content of dissolved calcium and magnesium compounds in water defines the water hardness. The bigger its proportion, the harder the water. Calcium and magnesium are therefore also denoted as hardening agents. The hardness is specified in millimol per liter (mmol/L) earlier, people preferred the degree of German hardness (°dH). According to § 9 of the detergent law (WRMG; Washing and cleaning agents law in the version of notification dated 17the July 2013 (BGBl. I S. 2538), which was amended last by Article 3 of the law dated 18th July 2017 (BGBl. I S.2774)) water is divided into three hardness ranges: above 2.5 mmol/L water is considered to be “hard”.

On heating or vaporizing hard water, the hydrogen carbonate forms $CaCO_3$ as in the carbonate equilibrium displayed above. In water pipes or heater rods, there is calcite build up, which is denoted as **slice**. [www.seilnacht.com/Chemie/ch_caco3.htm (08.06.2018)]

From an ocean depth of 3,500 m - the so-called calcite compensation depth, calcite dissolves fully in water. That is why at these depths, you find neither calcite-containing sediments nor clamp shells or skeletons. [www.seilnacht. com/Minerale/calcarag.htm (08.06.2018)]

Aragonite

Unless something else is specified, the following statements were taken on 08.06.2018 from https://www.mineralienatlas.de/lexikon/index.php/MineralData?lang=de&mineral=Aragonite as well as http://www.steine-
: Aragonite is a frequently occurring mineral from the mineral class of carbonate. It crystallizes in different shapes (see table 3.1): Prismatic crystals occur just as mineral aggregates, which can be spherical, oolitic striped, column-like and dendritic (plant type) as well as in parallel fiber form, radiating or needle-like.

In its pure form, Aragonite is colourless and transparent. Due to multiple refraction attributable to lattice defects or polycrystalline shape, it can also look white. Aragonite is the name-giving mineral of a group of minerals of similar structure and/or composition, the Aragonite group (found first in “Aragonia“).

Occurrence: in caves of volcanic stones, in the oxidation zone of mineral deposits (Aragonite flos ferri); as precipitation in sea water (Red Sea); in sulfur deposits (Mount Etna); as precipitation in sources; the shells of many clamps and snails consist of Aragonite.
[http://www.seilnacht.com/Minerale/calcarag.htm dated 08.06.2018]

Several colour and shape varieties of Aragonite exist:

- *Flos ferri*: Coral type growth in overwhelmingly white or whitish-gray colour; on rare occasions, light blue to pale blue-green flos ferri can also be found
- *Pea stone* or even *Pisolith*: mostly concentric shells or radiating spehres in predominantly whitish gray colour
- *Nicholsonite*: through admixtures of Smithsonite ($Zn[CO_3]$) mostly white, yellowish, green or light pink colour
- *Pea stone*: wave shaped, mostly white, gray, yellowish or red striped calc sinter
- *Sr-Aragonite*: strontium-containing Aragonite
- *Tarnowitzite*: through finely distributed inclusions of cerrusite ($Pb[CO_3]$) mostly white, gray to black or yellow coloured

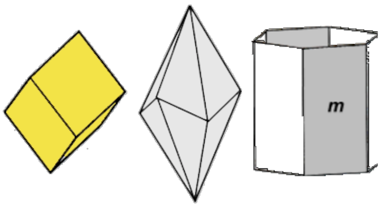
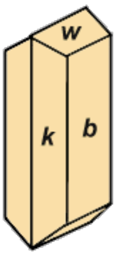
Aragonite is meta-stable under normal environmental conditions (20 °C and atmospheric pressure), the stable phase is calcite. To convert aragonite into calcite, the presence of solvent or the exercise of a relatively low pressure is sufficient, e.g., in a mortar.

Aragonite is hardly segregated in sweet water, the individual occurrences are characteristic of marine milieus. As magnesium favours the formation of aragonite as compared to that of calcite, in marine environments there is a preponderance of aragonite today. In addition to magnesium, traces of other metals like strontium, lead, barium and calcium sulfate as well as temperatures above 50 degrees celsius shift the balance towards aragonites.

Aragonite is the main component of the mother-of-pearl and therefore, of the pearl. Even the skeleton of stone corals consist of aragonite.

Table 3.1 Comparison of calcite and aragonite

Characteristics	**Calcite**	**Aragonite**
	 Calcite crystals are prone to be thick and round, as in these canon spar from Zacatecas.	 Aragonite crystals are frequently needle sharp. In this grade from Mexico aragonite grows on calcite.

Growth conditions	Calcite forms during the gassing of CO_2 from the watery calcium hydrogen carbonate solution.	Magnesium ions in the crystallization solution prevent calcite growth and favour the growth of Aragonite.
Composition	Calcium carbonate ($CaCO_3$) often manganese contents, but also mixtures with other carbonates, frequently traces of lead, iron, zinc, barium strontium or cobalt	Calcium carbonate ($CaCO_3$) Very few impurities of other elements available.
Solubility in acids	In acids like hydrochloric acid under flare and development of carbon dioxide CO_2: 	Also forms CO_2 with acids, but dissolves better than calcite in carbonic acid containing water. The better solubility of aragonite enables a chemical proof.
Crystal system	Trigonal system	Orthorhombic system
Crystals	Crystals occur frequently, the three basic shapes rhombohedron, scalenohedron and prisms are typical, there are numerous shapes:  Rhombohedron Scalenohedron Prism	Well-developed crystals with good recognition prisms. Pinakoidals and dipyramids are rare, mostly you will find needle-shaped or stalactite units.  
Twins	Twins occur in calcite in many forms and are collected as treasure: 	Aragonite is often twinned, as in this drilling from Minglanilla in Spain: 

[http://www.seilnacht.com/Minerale/calcarag.htm] vom 08.06.2018

Vaterite

If something else is not stated expressly, the following arguments were extracted on 08.06.2018 from https://www.chemie-schule.de/KnowHow/Vaterit : Vaterite a very rarely occurring mineral also from the mineral class of carbonate. It crystallises in the hexagonal form and develops only small, fibrous to prismatic crystals with hexagonal habitus up to approx. 0.1 mm or spherolithical units. Vaterite is formed through hydro-thermal separation at low temperatures in mineral-rich sources, but also in organic tissues: Component of gall bladder and kidney stones. Accompanying minerals are tobermorite and kaolinite, besides calcite and aragonite.

Other carbonate minerals

Besides calcites, aragonites and vaterite described in detail above, these include

- Smithsonite: $ZnCO_3$ (zinc carbonate),
- Dolomite: ($CaCO_3 \cdot MgCO_3$) and
- Cerrusite: $PbCO_3$.(lead-II-carbonate; white lead ore)

Smithsonite

The following information has been extracted on 08.06.2018 from www.steine-und-minerale.de/atlas.php?f=2&l=S&name=Smithsonit : Smithsonite ($ZnCO_3$, zinc carbonate) is also denoted as zinc spar or noble metal calamine. It crystallises trigonally, in the pure form it is colourless and transparent. Multiple refractions due to lattice faults or poly-crystalline formation can also make it look transparent white.

Along with other calamine minerals, smithsonite was treated as a zinc supplier for the manufacture of brass via a cementation process (that converts to gas through heating and the zinc released from the calamine evaporates on copper plates and forms brass as alloy).

Dolomite

The discussions have been taken from http://www.steine-und-minerale.de/atlas.php?f=3&l=D&name=Dolomit%20(Gestein) on 08.06.2018: Dolomite stone consists of minimum 90 percent mineral dolomite: chemical formula $CaMg(CO_3)_2$, ($CaCO_3 \cdot MgCO_3$). If the dolomite content is less, there is presence of a dolomitic lime stone. Dolomite stone is ideally white, frequently of the colour of ebony, light gray, yellowish gray or greenish gray. Dolomite stones emerged through the primary precipitation of dolomite or through the secondary dolomitization of lime sludge. Latest research shows with the help of recent examples of lagoons in Brazil the significance of sulfur bacteria and putrefaction for the dolomite genesis. [Krause et al.: *Microbial nucleation of Mg-rich dolomite in exopolymeric substances under anoxic modern seawater salinity*. New insight into an old enigma. In: *Geology 40*. No. 7, 2012].

Granulated dolomite is used in water treatment as silisic acid-free (SiO_2-free) filter material. For other different use areas in water treatment, dolomite is used at approx. 900 °C from dolomite ($CaMg(CO_3)_2$) to burnt dolomite ($CaMgO_2 = CaO \cdot MgO$). At lower combustion temperatures, there is a semi-burnt dolomite ($CaCO_3 \cdot MgO$) also called *Magno*, which is used in drinking water treatment for acid removal (compound of excessive CO_2). Here, preferably the MgO components react favourably.

Cerrusite

If something else is not mentioned expressly, the following discussions were taken on 08.06.2018 from https://www.edelsteine-mineralien-gemotion.at/mineralien/cerrusit/ : Cerussite, also called white lead ore, is lead-II-carbonate from the chemical point of view. Cerussite crystallises orthorhombically and mostly develops prismatic, latticed or pyramidal crystals, but also fine-grained powdery aggregates.

Cerussite is a typical mineral in the oxidation zone of carbon-containing lead deposits and comes from other galenites (lead shine). Here it is also found in combination with minerals such as smithonite (see above), but also anglesite, malachite, hemimorphite, and pyromorphite.

With the latter, it forms white-gray to brown coats which are known as lead soil. Black coloured cerussite (see above) of finely distributed lead shine is called black lead ore.

Other known carbonates are:

- Ammonium carbonate: $(NH_4)_2CO_3$, known as bicarbonate
- Phosphorus carbonate: K_2CO_3, known as potash
- Magnesium carbonate: $MgCO_3$, known as magnesia (magnesite)
- Sodium carbonate: Na_2CO_3 , known as soda or washing soda
- Sodium hydrogen carbonate : $NaHCO_3$, known as sodium bicarbonate (baking soda)

Discussion on the origin fo water-soluble carbonates – starting point of hard water

The alkali carbonates dissolve well in water, while the others are poor solvents. The water solutions react strongly as alkalies: The carbonate ion CO_3^{2-} reacts as base with a water molecule, with a water molecule of a hydrogen carbonate ion and a hydrogen ion:

$$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$$

With strong acids, the carbonate and hydrogen carbonate disintegrate under the formation of carbon dioxide and the corresponding salts. Sodium carbonate e.g., with with hydrochloric acid to sodium chloride, water and carbon dioxide:

$$Na_2CO_3 + 2\,HCl \longrightarrow 2\,NaCl + H_2O + CO_2$$

Calcite and aragonite formation during the heating or vapourization of water

While earlier it was considered predominantly how the separation of $CaCO_3$ took place, (bio-geomorphologically), chemically in the past, now it should be considered what emerges from the dissolved carbonates in drinking water and industrial water, if calcium containing water is heated, in which the dissolved hydrogen carbonates (as sketched above) are located:

$$Ca^{2+} + 2\,HCO_3^- \rightleftharpoons CaCO_3 + H_2O + CO_2 \quad \text{(carbonate equilibrium)}$$

During heating or vapourization of hard water, $CaCO_3$ is formed as displayed in the carbonate equilibrium cited above. In water pipes or heater rods, normally there is calcite formation, also denoted as **slice** [http://www.seilnacht.com/Chemie/ch_caco3.htm (08.06.2018)].

This is a common observation in all text books. What has not been considered by far is what Coetzee et al., [Coetzee P.P., M. Yacoby, S. Howell (1996) *The role of zinc in magnetic and other physical water treatment methods for the prevention of scale.* Water SA 22 p. 319-326] has published on the influence of metals in water, as they studied the observed effects of physical and especially magnetic water treatment systems: The authors determined at that time that traces of zinc that detached themselves from the magnets and metallic surces of the housing were sufficient for “the nucleation rate of calcium carbonate slow down and also promote its crystallisation in the aragonite rather than the calcite form even under conditions where calcite would be the preferred crystal form.“

In 1998 Coetzee et al. of the Department of Chemistry and Biochemistry, Rand Afrikaans University, PO Box 524, Johannesburg 2006, South Africa [Coetzee P.P., M. Yacoby, S. Howell and S Mubenga (1998) *Scale reduction and scale modification effects induced by Zn and other metal species in physical water treatment,* Water SA Vol. 24 No. 1 January 1998 p. 77-84] quantified: “A minimum Zn/Ca mass ratio of 0.06 x 10^3 was required for Zn to cause measurable effects. At Ca > 300 mg/L addition of Zn of up to 100 mg/L had a negligible effect on nucleation rate and crystal morphology. Cu was found to be only half as effective as Zn while Mg required to be present at concentrations 1.000 times more than Zn to produce comparable effects. Colloidal Fe_2O_3 caused a decrease in induction time. The direct effect of Zn on scale reduction in laboratory tests amounted to about 77 ± 6 % and was achieved with 300 mg/L Ca solutions to which 200 mg/L Zn was added.”

Werner, A. examined in 2008 the AQUABION® AB-S15 in lime containing drinking water [*Tests on the effectivity of chemical and physical water hardening*, research paper Alexander-von- Humboldt High School, Schweinfurt, college level 2008] and found after a 30-minute circulation through the AQUABION® AB-S15 in REM pictures, conspicuous changes in the morphology of the crystals (Fig. 3.1a and b): "Instead of several smaller units, there are now many small units as well a few specially large lime crystal units, which have a diameter of nearly 100 µm.

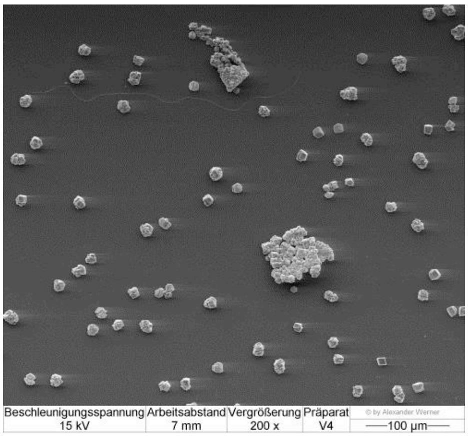


Figure 3.1a 200x enlarged

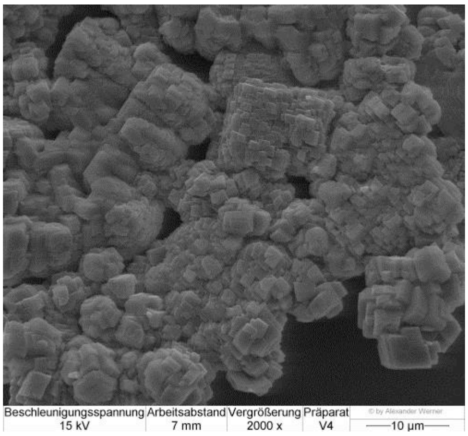


Figure 3.1b 2,000x enlarged

Similar observations can be made at home, when one buys a new water boiler: The hotplate made of stainless steel elutes sufficient metal ions in the beginning (see Graphics 2.1 above), which separates calcium carbonate in small plate type or ball shaped units and does not form a crust as slice (calcite) on the exchanger surface, so that it can be wiped off or discharged from the pipes along with the water flow.

If one accepts the figure of Coetzee et al. (1998) of 0.00006 Zn ions in the ratio 1 Ca ion as given, then it means that a Zn-ion leads to the fact that 16.000 Ca ions are changed to the aragonite form of the calcium carbonate.

Freij et al. [Freij, S. J., A. Godelitsas, A. Putnis: *Crystal growth and dissolution processes at the calcite-water interface in the presence of zinc ions*, Journal of Crystal Growth 273 p. 535-545 (2005) has described that the deposition of zinc at calcite surfaces strengthens aragonite formation.

4 Corrosion of metals, especially zinc and along the electo-chemical series

"Corrosion is the reaction of metallic substance to the environment, which results in a tangible change in the substance … . In most cases, the reaction is of an electro-chemical nature, but in some cases, it can also be chemical or physical-metallic by nature. [According to DIN EN ISO 8044 Corrosion of metals and alloys – basic terms: (www.din.de/de/norm- entwurf/din-en-iso-8044/224898155) (Version 02-2015)]. Corrosion is always a corrosion system which is influenced mutually (s. graphics 4.1).

Graphics 4.1 Corrosion system [Lecture Galetz, 2014, www.metalle.uni-bayreuth.de/de/download/teaching_downloads/Vorl_Metalle2/Lecture-Bayreuth_WS2014_waessrige-Korrosion.pdf]

On metallic surfaces, water always leads to chemical and electro-chemical reactions in which metal ions dissolve in the solution, depending on the temperature, the pH-value, the chloride content and other present metals with which the galvanic element is formed. A role is player here by the electro-chemical “series of the metals “: Graphics 4.2.

The electro-chemical series (RedOx series) is a listing of RedOx pairs according to their standard electrode potential (= RedOx potential under standard conditions. The RedOx behavior of a substance can be derived from the electro-chemical series. Each RedOx reaction is described through two pairs; one can predict the direction of reactions from the electro-chemical series.

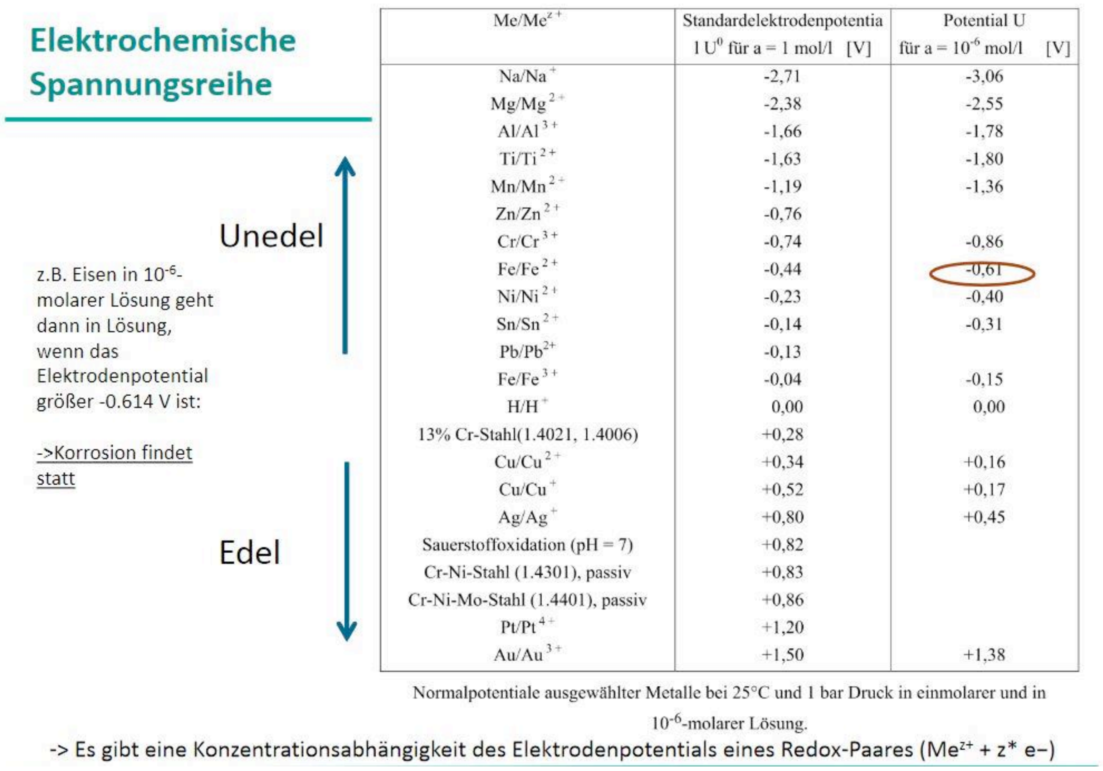
In metals, the metal itself and its associated ion build a RedOx pair:

Red… …**ox** + z e$^-$

For example

Cu   Cu^{2+} + 2 e$^-$

Cu is the reduced form (“Red…“) and Cu^{2+} the oxidized form (“…ox“). The RedOx potential specifies a measure of the readiness of the ions to accept the electrons. The ions of noble metals accept willing electrons much more than the ions of non-noble metals, because of which under standard conditions the RedOx potential of the Cu/Cu^{2+} pair at +0.35 V is clearly more positive than that of Zn/Zn^{2+} pair at −0.76 V. This means that Zn (non-noble) is a strong reduction agent, i.e., its reaction participants are reduced and it itself is oxidized and gives up electrons (for example, if one dips a Zn bar in a Cu^{2+} salt solution, the zinc atoms oxidize to zinc^{2+} ions through electron surrender, which go into the solution, while the copper^{2+} ions are reduced in the solution with the help of the released electrons, and separate on the zinc sheet. The copper layer however, cannot prevent the zinc bar from dissolving further.



Elektrochemische Spannungsreihe

Unedel

z.B. Eisen in 10^{-6}-molarer Lösung geht dann in Lösung, wenn das Elektrodenpotential größer -0.614 V ist:

->Korrosion findet statt

Edel

Me/Me^{z+}	Standardelektrodenpotentia 1 U^0 für a = 1 mol/l [V]	Potential U für a = 10^{-6} mol/l [V]
Na/Na$^+$	-2,71	-3,06
Mg/Mg^{2+}	-2,38	-2,55
Al/Al^{3+}	-1,66	-1,78
Ti/Ti^{2+}	-1,63	-1,80
Mn/Mn^{2+}	-1,19	-1,36
Zn/Zn^{2+}	-0,76	
Cr/Cr^{3+}	-0,74	-0,86
Fe/Fe^{2+}	-0,44	-0,61
Ni/Ni^{2+}	-0,23	-0,40
Sn/Sn^{2+}	-0,14	-0,31
Pb/Pb^{2+}	-0,13	
Fe/Fe^{3+}	-0,04	-0,15
H/H$^+$	0,00	0,00
13% Cr-Stahl(1.4021, 1.4006)	+0,28	
Cu/Cu^{2+}	+0,34	+0,16
Cu/Cu$^+$	+0,52	+0,17
Ag/Ag$^+$	+0,80	+0,45
Sauerstoffoxidation (pH = 7)	+0,82	
Cr-Ni-Stahl (1.4301), passiv	+0,83	
Cr-Ni-Mo-Stahl (1.4401), passiv	+0,86	
Pt/Pt^{4+}	+1,20	
Au/Au^{3+}	+1,50	+1,38

Normalpotentiale ausgewählter Metalle bei 25°C und 1 bar Druck in einmolarer und in 10^{-6}-molarer Lösung.

-> Es gibt eine Konzentrationsabhängigkeit des Elektrodenpotentials eines Redox-Paares (Me^{z+} + z* e−)

Graphics 4.2 Electro-chemical series of metals [Lecture Galetz (2014)] The electro-chemical series entered in short for the selected series:

K < Na < Mg < Al < Zn < Sn < Pb < Cu < Ag < Au

It is apparent from Graphics 4.2 that zinc goes into the solution before lead and copper and consequently, if one creates a galvanic element made of zinc and copper, zinc switches to the dissolved form.

In the dissolved state, zinc is present as $ZnOH^+(aq)$ or as $Zn^{2+}(aq)$. Even the form of $ZnCO_3$ (solubility 0.21 g/L) is encountered.

The water temperature strengthens the surface attack (the “fist rule” applies: For every temperature increase by 10 Kelvin (10 °C) the reaction speed increases to its double).

For hot galvanized steel pipes, the pH-value is more important: Low pH-values under 6.9 lead to faster zinc discharge while higher pH values from 7.9 besides low corrosion rates encourage the formation of effective protection layers [Rückert, J.: *Influence of the pH-value, the oxygen content and the flow speed of cold drinking water on the corrosion behavior and the protective layer formation in hot galvanized steel pipes*, substances and corrosion 30, P. 9-34, Verlag Chemie, GmbH, Weinheim (1979)].

In the corrosion system “zinc in water“ high oxygen and carbonic acid concentrations and high salt concentrations of chloride, sulfate and nitrates play a corrosion-enhancing role. In a school experiment with hydrogen splitting mineral acids, diluted hydrochloric acid (HCl) with 1 mol/L displays the reaction (in Fig. 4.1), how fast and how much hydrogen (H_2) is formed if one places zinc sheet in the diluted HCL solution [www.seilnacht. com/Lexikon/reaktge.htm vom 12.06.2018]:

$$2\ HCl + Zn \dashrightarrow H_2 + ZnCl_2.$$

The concentration of hydrochloric acid falls initially with 0.2 mol/L*min. The H_2 production remains stöchiometric in relation to zinc dissolution. It depends on the concentration of the reaction partner (it would be higher for zinc powder due to the bigger surface as compared to zinc sheet).

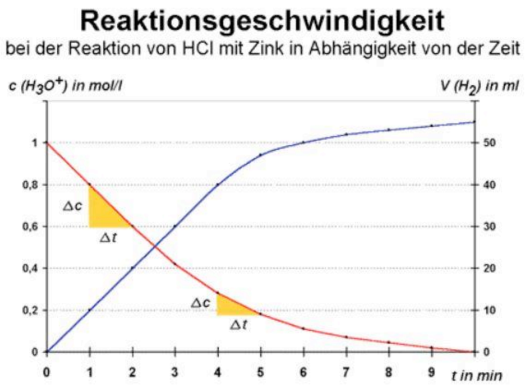


Figure 4.1 Hydrogen formation from HCL solution with zinc sheet inserted [http://www.seilnacht.com/Lexikon/reaktge.htm dated 12.06.2018]

The age of the galvanized pipe (duration of integration) and stagnation of the water in galvanized pipes has an influence on the zinc concentration in water. On one hand there is corrosion, on the other hand there is a cover layer formation: Rückert (1979) determined that the pH-independent oxygen content and flow speed lead to initial corrosion. After a very short duration however, it then leads to a microscopic layer made of hinc hydroxide, which leads to a very strong reduction of the corrosion speed. The dissolution speed of a zinc hydroxide layer and therefore, the re-dissolution speed of a zinc hydroxide layer and with it the corrosion speed is determined later from the pH-value and the flow speed, after the zinc hydroxide layer stabilizes after a carbonate conversion, so that a further release of zinc at the phase limits of the zinc hydroxide layer/water remains undone.

A transportation of zinc ions in the watery environment takes place through the so-called “pore mechanism“[Rückert (1979)]. Certain exchange operations through pore diffusion in the macroscopic layer are extremely complex, because they depend dynamically on the concentrations at the hydrogen ions and hydrogen carbonate ions.

But with increasing time, the corrosion speed drops. For a good long-term protective action of the final cover layers. It is assumed that the conversion, i.e., the zinc release in the macroscoplic primary layer takes place slowly, that a successive replacement of the released zinc-containing substance through water content substances calcium, silicium, phosphorous and iron coming from the pipe material can take place and therefore, a further thick, strong bonding cover layer remains intact – a case which is not possible at low pH values [Rückert (1979)]. This effect is reinforced, if the pores are clogged by deposits of water-containing substances and integration of iron compunds, especially observed at high initial pH values.

The influence of flow speed on the corrosion operations, the cover layer formation and conversion return to the mass to the extent the pore transport operations reduce speed with increasing thickness of the cover layer, because changes in fluid diffusion layer have less side effects on the transport operations as compared to the essentially bigger obstructions in the cover layer.

Case example (Table 4.1):

For the testing of zinc released from zinc pipes, Rinck [Rinck, A.: *On the usability of solid zinc pipes for water pipe purposes*, magazine for testing food and luxury food, also see applied chemisty, Volume 27, p. 72-75, published online: 18th January (2006)] a cut piece of zinc pipe which is 48 cm long, has a clear width of 26 mm and a coat diameter of 3 mm. The zinc pipe was cleaned on the inner and outer sides mechanically till it had a shining metal surface and then placed in a glass pot with lockable stationary cylinder of 1 litre capacity, and flushed with water. The time for which the water came in contact with the zinc pipe was 1, 2 and once 8 days. Before each test, the outer surface was polished to restore the metallic shine to remove possible cover layers (in one test approach, there was no friction to be able to determine whether a formed layer has any relation to the release behaviour).

Table 4.1 Zinc discharge from zinc pipe (determined colorimetrically) [Rinck, A. (2006)]

Test	Type of used water	Duration in days	Zinc [mg/L]
1	Destilled water	1	20
2	Pipe water from city water works (7.4 dH)	1	12
3	Carbonic acid containin water	1	150
4	Distilled water	2	50
5	Pipe water from city water works (7.4 dH)	2	14
6	Carbonic acid containin water	2	280
7	Pipe water from city water works (7.4 dH)	8	20

The following can be detected from Table 4.1:

1. The quantity of the dissolved zinc increases with the duration of the effect, though not proportionally.
2. With the increase of free carbonic acid, the zinc removal rate increases too.
3. In case of long-term effect, a cover sheet system builds up, which reduces the separation of zinc.

4. Destilled water dissolves larger quantities of zinc than pipe water, although it does not contain any carbonic acid and has a pH-value of 7. Distilled water immediately accepts CO_2 in contact with the environmental air and the pH-value decreases fast to 5.

From a zinc content of approx. 50 mg/L, the water has an opalizing to milky turbid appearance. During the course of one year, the zinc solubility during stay in pipe water for longer periods reduced to 2-3 mg per litre [Rinck, A. (2006)].

Woon, K.H. and C.X. Qi tested in 2007 [A Study of Effectiveness of Galvanic Water Treatment, Singapore Polytechnic School of Building Environment Diploma Work] zinc contents for over 9 weeks in two water circulation systems (with and without AQUABION®) and determined that the zinc concentrations with the sacrificial anode system were invariably higher than in the comparison system (s. Fig. 4.2).

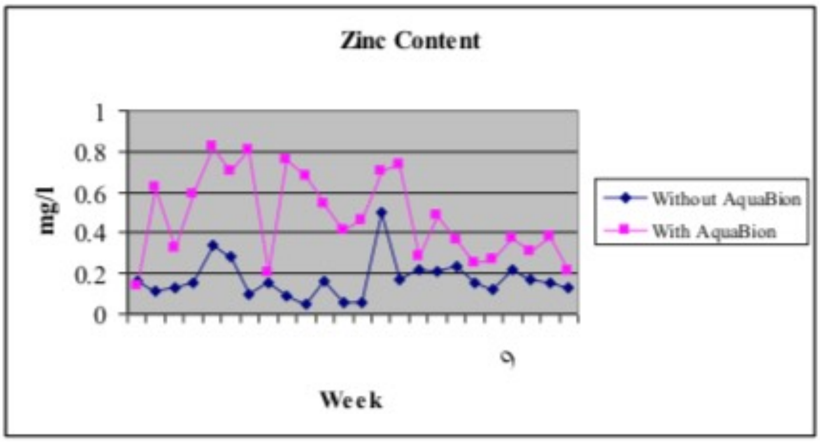


Figure 4.2 Process of zinc concentration in two identical water circulation systems without and with the sacrificial anode ssytem (AQUABION®) [Woon, Qi (2007)]

5 Water circulation systems – scaling and bio-fouling processes

Cold water circulation systems are characterized by the fact that they have two determining inputs (see Figure 5.1):

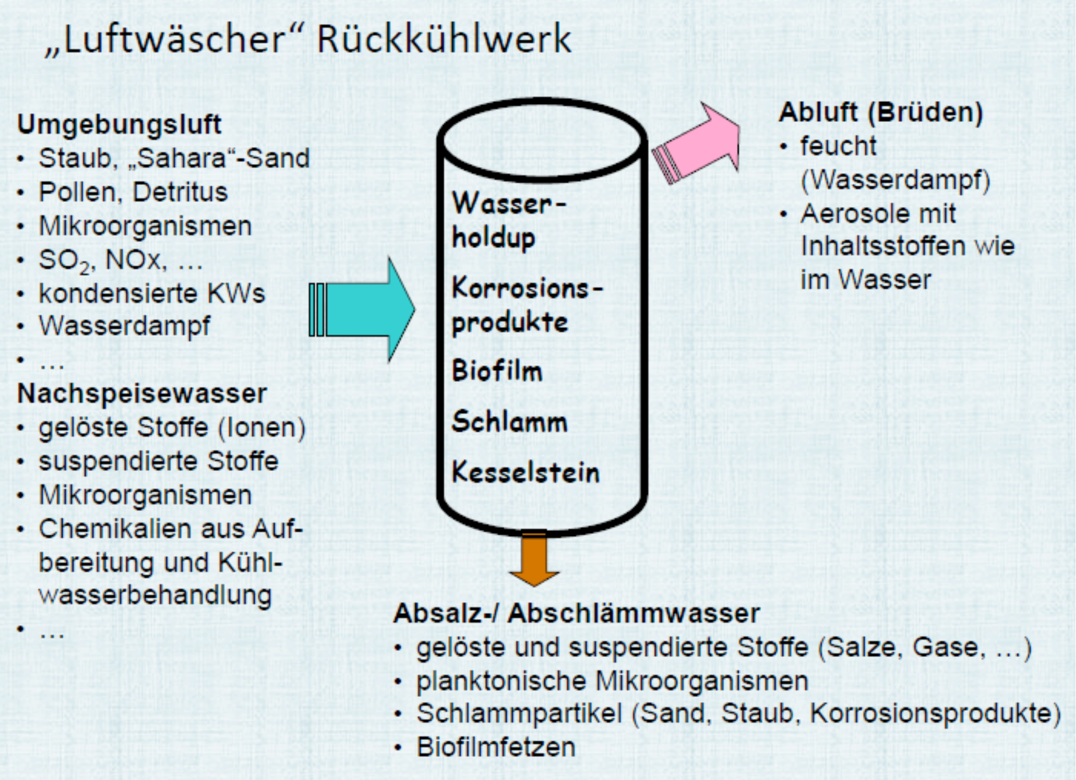
1. The post feed water and
2. The environmental air input.

Cooling water circulation systems with open heat exchangers should be considered to be washer of the environmental air [Kunz, P.M.: Legionellen, TAE-Seminar on heat exchanger systems (Jan. 2017).

Cooling is a thermodynamic process in which heat or thermal energy is extracted from a system – This gives rise to the cooling. The heat is absorbed by the atmospheric air (the heat carrier). In too many processes in industry, process heat is transferred to the heat carrier water, which is then cooled in a heat exchanger system with the help of air, so that the heat carrying water can be used multiple times in the circulation. The heat-exchanging system is often operated via a cooling tower to cut costs.

The quality of the used water determines the expenditure one must incur to be able to operate the open cooling sytem; the system has one more input: the atmospheric air. The cooling tower too is "unfortunately" an atmospheric air washer. Hence, gaseous and solid substances from the atmospheric air are discharged in the heat exchanger system. The operator of an open heat exchanger therefore, must always perform a cooling water treatment. Through the vapourization of the water, the non volatile substances concentrate in the water. Frequently, the substances are dozed, which prevents scaling (= formation of crust on the heat exchanger surfaces). Mostly, a certain part of the cooling water is de-sludged (desilted) and replaced by fresh back feed water

Besides, corrosion protection materials to protect the metallic pipes and conservation materials are dosed to limit the biofilm growth at the heat exchanger surfaces, because it prevents heat transfer.



„Luftwäscher" Rückkühlwerk

Umgebungsluft
- Staub, „Sahara"-Sand
- Pollen, Detritus
- Mikroorganismen
- SO_2, NOx, ...
- kondensierte KWs
- Wasserdampf
- ...

Nachspeisewasser
- gelöste Stoffe (Ionen)
- suspendierte Stoffe
- Mikroorganismen
- Chemikalien aus Aufbereitung und Kühlwasserbehandlung
- ...

Wasser-holdup

Korrosions-produkte

Biofilm

Schlamm

Kesselstein

Abluft (Brüden)
- feucht (Wasserdampf)
- Aerosole mit Inhaltsstoffen wie im Wasser

Absalz-/ Abschlämmwasser
- gelöste und suspendierte Stoffe (Salze, Gase, ...)
- planktonische Mikroorganismen
- Schlammpartikel (Sand, Staub, Korrosionsprodukte)
- Biofilmfetzen

Figure 5.1: Stock input-output analysis for a cooling tower [Kunz, P.M. (2017)]

Wherever water is charged with traces of organic, but also inorganic substances, there are unavoidable living microorganism developments due to chemical and photosynthesis processes, as one can detect in open cooling water systems in the form of biofilm in beautiful greenish brown optics:

One then speaks of bio-fouling (see Figures 5.2 a and b).

Figure 5.2 a and b: Biofilms at and in heat exchanger system [Kunz, P.M. (2017)]

Scaling and bio-fouling lead to reduction of heat transfer rate, the biofilms serve as nesting grounds for disease spreaders, especially for the dangerous legionella, which breed in employee workplaces and is distributed in the environment after multiplying into large masses in the heat exchanger system.

A precondition for the bio-film formation is that firstly, microorganisms are present (they come from the backfeed water, predominatly however, from the air (see Fig. 5.1) and secondly, energy and construction material sources (which also come from the air, but also from the used water itself and the chemicals for back feed water treatment or cooling water circulation water treatment. Thirdly, it must be maintained that the ecological master conditions must allow a growth. In open cooling water systems, all components are mostly available for scaling and microbial settlement to thrive:

Microorganisms always live in cooling water circulation systems – in the flowing phase as well as in the dead spaces and on the walls of the pipes in more or less thick biofilms, depending on the flow reroutings. They multiply based on the nutrition supply; they become more and more “stress resistant”, depending on the type and frequency of biocide usage – and are not “small” to catch.
All of us, who brush our teeth daily (several times) know that an existing biofilm cannot be removed fully from the system (as during brushing of teeth: not even despite chemicals (toothpaste) and mechanism (brush) and flow (flushing and mouth wash).

Besides, the autotrophic microorganisms meet their building material demand through absorption of light energy and carbon dioxide assimilation during photosynthesis, the hetrotrophes through the acceptance and use of organic nutrition, where these are complex, mostly coupled conversion processes. This happens in the different cellular life systems predominantly according to the same or similar principles. But there are basic differences in their energy and building material supply, as Table 5.1 illustrates: Biomass build-ups are possible from any organic substances as long as CO_2 is available.

Tab. 5.1: Modes of nutrition of micro-organisms

Nutrition mode	**Energy source**	**Hydrogen source**	**Nutrition source**
chemo-organo heterotrophy	Organic substance	Organic substance	Organic substance
photo-litho autotrophy	Light	H_2O, H_2S	CO_2
chemo-litho autotrophy	inorganic substance	Inorganic substance	CO_2
photo-organo autotrophy	Light	Organic substance	CO_2

Chemo-litho autotrophic bacteria use all energy sources, inorganic oxidizable compounds like carbon monoxide, sulphide, ammonium and nitrate, bi-valent iron and hydrogen, while they reduce organic carbon compounds with the energy gained from them. The end products of this metabolism are sulphate, nitrate, trivalent iron and water, and organic biomasses. The organic compounds built thus can then be reused by hetrotrophic microorganisms, so that a continuous growth of biomass is to be expected. Interestingly, besides heterotrophic and autotrophic organisms, there are also other types that can use mixotrophic CO_2 and acetate (*Nitrobacter, Desulfovibrio vulgaris*). All organisms cannot build all the compounds necessary for the growth (vitamins, purine or pyramidine) themselves; these are then directed to other organisms. This process is actually limited if an essential food component (carbon, nitrogen or phosphorus) is at its minimum.

The formation of biofilms on surfaces cannot be clarified through a single mechanism alone. The growth is determined by three components:

- Microorganisms (species, microbial composition, number of cells, growth phase, nutrient status, surface charging, hydrophobicity).
- Surface (chemical compositon, surface tension, charging, roughness, hydrophilia).
- Water (temperature, pH-value, oxygen concentration, Redox potential, organic and inorganic contents, viscocity, surface tension, flow ratios).

To prevent microbial colonies in water circulation systems, or at least to restrict them, microorganisms are being combatted today; a large number of anti-microbial sustances are being added to water - some continuously, some [see KUNZ, P.M. and G. FRIETSCH. Microcide materials in biological clear systems. Springer- Verlag (1986)] at regular intervals. Once a biofilm builds up in a system, it is impossible to get rid of it permanently. Biofilm organisms are essentially insensitive to biocides, the cells in the interior or most of all in the consortia are protected.

- The microorganisms are protected in the biofilm.
- Surviving microorganism infect the system again.
- Dead microorganisms form a nutrient base for other microorganisms and encourage them to grow.

About Legionella, one knows now that they wash well in macrophages (anarobic) and can multiply because they are not attacked by the glazing digestive substances. The temperatures in cooling water circulation systems are often such tht the Legionella can wash well (around 45°C).

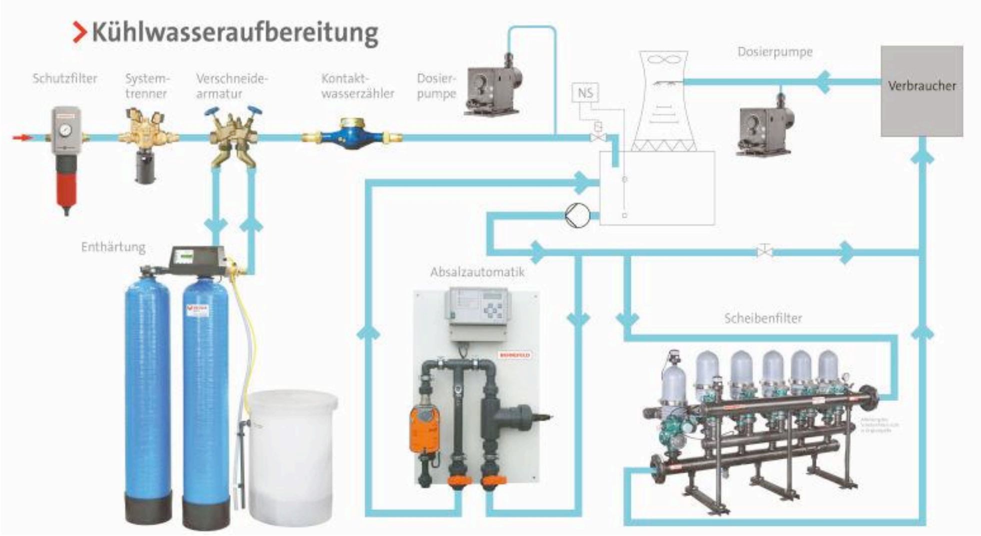


Fig. 5.3: Scheme of cooling water circulation with cooling water treatment
[http://www.veoliawatertechnologies.de/wasseraufbereitung/anwendungen/kuehlwasser_klimawasser/ vom 22.06.2018]

Cause of the wave of legionella diseases in “Warstein” with minimum two deaths is, according to the information we have thus far, a heat exchanger in a Warstein-based metal extraction company, which was fed by flow water from the Wester, and the aerosole from the local brewery sewage treatment plant [https://www.wp.de/staedte/warstein-und-umland/legionellen-experte-exner-hofft-auf- erkenntnisse-fuer-die-wissenschaft-id8484786.html vom 22.06.2018]. Examinations showed clearly that the legionella from the heat exchanger system were genetically identical to those that triggered the disease. Apparently, contaminated aerosols from the heat exchanger system were the cause of the disease cases. It should be interesting for all participants, that the heat exchanger of the company was infected with the legionella from the atmospheric air (see above) as well as via the flow water as backfeed water. The legionella multiplied and got distributed in the coolilng system due to the aersoles in the vapours.

There are many options of controlling heat exchanger systems:

1. One adopts the VDI 2047-2 and follows it.
2. And one prevents the biomass/biofilm building potential through technical bio process measures [Kunz, P.M.: Microbiological aspects in industrial waters in handicrafts, commerce and industry. DWA discussion on hygiene 2016]

6 The principle of AQUABION®

The AQUABION ® is a current-less working pipe fitting with an internal galvanic element, the core of which releases zinc ions from a zinc sacrificial anode system in the flowing water (s. Fig. 6.1).

The principle according to which it works is based on the mechanism of cathodic corrosion protection with external power. The objective here in most cases (as e.g., in water boilers) is to protect a metal which comes in contact with water from rust. Here, as mentioned above, one basically sacrifices a non-noble metal to protect the more valuable metal.

If one brings two such different metal bodies in contact through a water body, a current flows which is fed from the redox reaction of the oxidation to the sacrificing anode. The current is only a few milliamperes in strength.

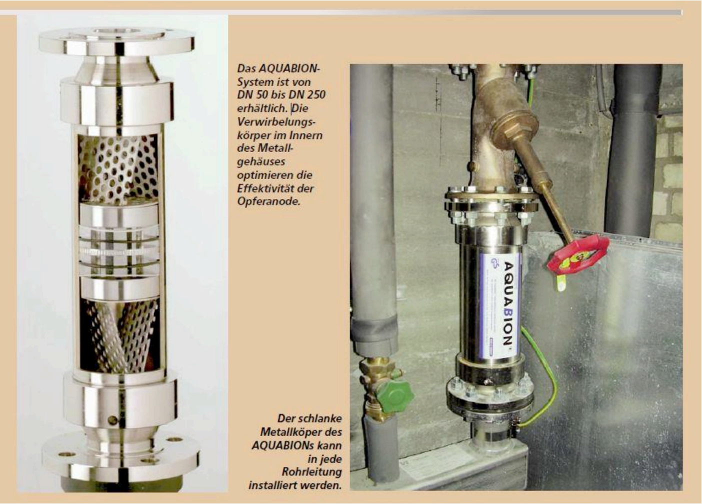
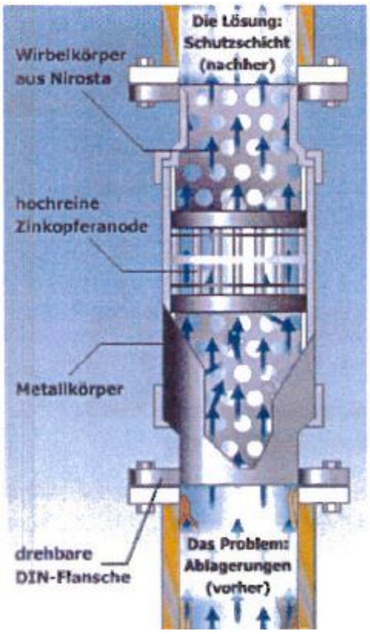


Figure 6.1a AQUABION® In the section (left) and in the centre of an integration view [Flettner, M.: *Cookies do not contain any lime*, www.tga-praxis.de Modern building technology 5 (2008)

Figure 6.1b AQUABION®in the section (right with details) Schilte, M.: *Function check of AQUABION® for water treatment*, LANXESS (o.J.)]



The reaction runs as follows (explained with the help of Zn-Fe): As soon as zinc or iron comes in contact with water, it is oxidized to Zn^{2+} or Fe^{2+}. Corresponding to the electro-chemical series mentioned above (see Fig. 2), there is a potential difference between the zinc and iron of 1.9 V (standard potentials at 25 °C; 101.3 kPa; pH = 0; ion activities = 1). As zinc has an essentially more negative potential with a potential difference with hydrogen of –2.38 V than iron –0.44, zinc is oxidized at the anode and the iron is reduced through the acceptance of electrons. The electrons split water into H_2 and 2 OH^-. The iron does not change as it can again accept electrons released by zinc. As against this, the zinc slowly dissolves.

In AQUABION®, the conducting compound between the brass housing and the zinc sacrificial anode with the flowing water is produced: A galvanic element with a cell voltage of approx 0.7 to 1.0 volt is generated, depending on the quality of the water [Werner, A. *Tests on the effectiveness of chemical and physical water softening*, Research paper Alexander-von-Humboldt High School Schweinfurt, A-Level 2008].

The zinc sacrificial anode switched upstream and downstream as diaplyed in Figure 6.1b right, are swirling bodies made of Nirosta (non-rusting steel). They are supposed to swirl suspended particles in water and grind the zinc sacrificial anode. This way a bigger contact area is to be created and maintanined.

It cannot be ruled out that the swirling body builds a galvanic element with the zinc sacrificial anode.

7 Test results of zinc release in AQUABION®

Internal test results with AQUABION® are given below which supplement the work of other research groups.

7.1 Test results on IBV for zinc release in AQUABION® [Kunz P.M., I. Sommer: “*Tests for zinc release of a sacrificing anode system,* STZ-IBV result report (dated 28.03.2008)]

- It can be summarized that the AQUABION® discharges zinc in considerable amounts in this medium not expected in this quantity: After 4 months of operation, there were still approx. 0.9 mg/L*d in the circulation water.
- It can be confirmed that the hardening agent (here CaO) is influenced in such a way that they do not separate essentially on hot surfaces.
- It appears that – a definitive statement is not possible due to the passivization of the surfaces with the passage of time and the counter developments in the medium –, that more zinc is released in the medium with increasing hardness and increasing pH value.

To get a basis for the discharge of zinc release of AQUABION ® under different process conditions, the test series reproduced in Table 7.1-1 was conducted to determine the influence of possible zinc discharge sources (metal strap of the pump, metallic thermometer of the pH value measuring probe, zinc content fluctuations in VE water etc.). Some quantitative results of the tests are reproduced below.

Table 7.1-1 Summary of the preliminary tests [Kunz, P.M., I. Sommer (2008)]

Test No.	Test	Result
U-1	Analysis of pure water on zinc content and hardness	Baseline zinc content and hardness of the used pure water.
U-2	Tests with artificial adjustment of the degree of hardness	Artificial adjustment of a hardness degree with CaO is possible. The CaO must be released through the bubbling of CO_2.
U-3	Zinc discharge during integration of AQUABION® with steel pipe connections.	Steel accounts for a solid discharge of zinc in the system.
U-4	Test of zinc discharge when using copper pipes and plastics without AQUABION®	The peripheral zinc discharge could be reduced by using copper pipes instead of steel pipes.
U-5	Influence of extraction duration of the pure water on the zinc content	The period of extraction does not have any influence on the zinc content of the pure water.
U-6	Influence of the metallic thermometer and pump on the zinc discharge	Start up (use of a metallic thermometer and runtime of the pump before test start) causes a considerable amount of zinc to be discharged in the system. It is therefore necessary to measure the starting content of zinc before each test.
U-7	Zinc discharge of AQUABION®s in connection with copper pipes	The zinc discharge is in the mg range, so that the zinc concentration can be determined via cuvette tests.

Tests of zinc discharge during integration of AQUABION® with steel pipe connections

Figure 7.1-1 shows the structure of the test: the AQUABION® was installed with the help of two steel pipe sections and a few brass connecting pieces. 10 L hardened pure water was pumped in the hotbed for a defined time for different durations (s. Tab. 7.1-2). The zinc content of the water was then determined with cuvette tests of HACH-LANGE.

Table 7.1-2 Results of the test of zinc discharge of AQUABION® during intergration with steel pipe sections

[Kunz, P.M., I. Sommer (2008)]

Duration of test	Zinc (mg/L)
1 day at pH 6, 40°C and 9.6°dH	9.69
1 day at pH 6, 40°C and 13.6°dH	10.9
1 day at pH 6, 40°C and 19.2°dH	7.86
1 day in VE- wasser	3.07
4 days, VE water only	6.17

The results indicated that by connecting AQUABION® with steel pipes, brass connecting pieces lead to a solid discharge of zinc in the unpumped water, which does not come from the AQUABION® alone.

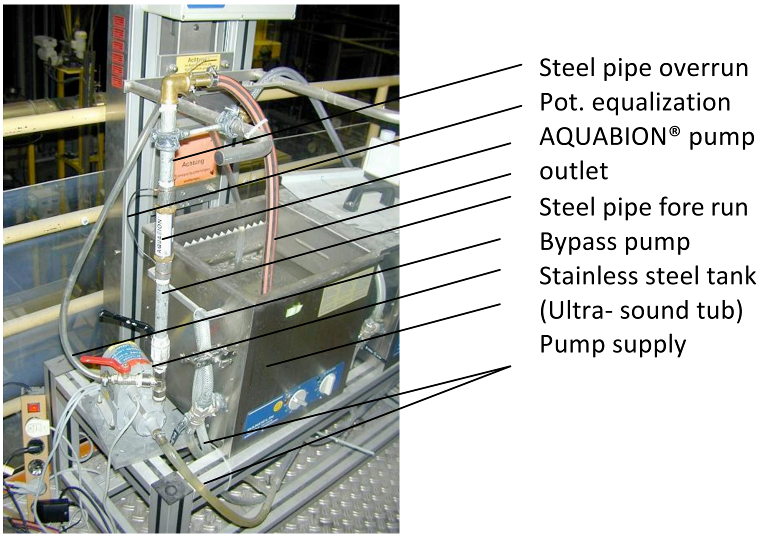


Figure 7.1-1: Test structure with AQUABION® + steel pipe connections [Kunz, P.M., I. Sommer (2008)]

Test of zinc discharge when using copper pipes and plastic connectors (without AQUABION®)

A 20 L glass aquarium was used as container, which was filled with 10 L hardened pure water. The pH-value was adjusted with HCl to 6.0, the water was heated with the help of an external heated bath to 40 °C and the water was pumped for 23 h. The volume flow of the pump was 2.5 L/min (150 L/h). The zinc content of the water was then determined.

The tests – reproduced in Table 7.1-3 – show that the test structure does not have any influence on the water hardness, the zinc content however increased by 0.53 mg/L. The conductivity increased by approx 10 µS/cm, while the pH-value fell from 6.1 to 4.8.

Table 7.1-3 Result of the test on zinc discharge on using copper pipes and plastic connectors without AQUABION®

Date	pH	Conductivity [µs/cm]	Temperature [°C]	Zinc [mg/L]	Hardness [°dH]	Ca [mg/L]	Mg [mg/L]

[h]							
0	6.1	39.1	39.7	< NG (0.156)	0.85	6.0	< NG
0.5	5.7	39.4	41.2	-	-	-	-
1.0	5.3	39.9	42.0	-	-	-	-
1.5	5.2	40.5	42.0	-	-	-	-
2.0	4.9	41.0	41.6	-	-	-	-
22.0	4.8	49.7	39.8	-	-	-	-
23.0	4.8	49.7	39.5	0.688 (double determination)	0.86	6.1	< NG

The decrease in pH value is attributable to the release of CO_2 from the air. By using copper pipes instead of steel pipes the peripheral zinc discharge could be reduced appreciably. The influence of the metallic thermometer and the pump on the zinc discharge could be determined at 0.04 mg Zn/d.

Test of zinc discharge on using copper pipes and plastic connectors with AQUABION®

Then AQUABION® was integrated in the system with two copper pipe connections in the piping system connected to the 20 L aquarium and the test series was resumed.
(At this point of time, the AQUABION® had already been in operation for 2 weeks so that the initial zinc discharge should have been arrested by the initial corrosion. Further in this test series, the thermometer of the pH measuring instrument was in use in the test for 23 h. The values specified in Table 7.1-5 were measured without the thermometer after the pH value adjustment.

Table 7.1-4 Results of the zinc discharge on using copper pipes and plastic connectors with AQUABION® [Kunz, P.M., I. Sommer (2008)]

Date	pH	Conductivity	Temperature	Zinc [mg/L]	Hardness	Ca [mg/L]	Mg [mg/L]
0	6.1	39.1	39.7	< NG (0.156)	0.85	6.0	< NG
0.5	5.7	39.4	41.2	-	-	-	-
1.0	5.3	39.9	42.0	-	-	-	-
1.5	5.2	40.5	42.0	-	-	-	-
2.0	4.9	41.0	41.6	-	-	-	-
22.0	4.8	49.7	39.8	-	-	-	-
23.0	4.8	49.7	39.5	0.688 (double determination)	0.86	6.1	< NG

Table 7.1-5 Results of the tests on zinc discharge of AQUABION® for connection with copper pipes at minimum contact time with the thermometer [Kunz, P.M., I. Sommer (2008)]

Date	pH	Conductivity	Temperature	Zinc [mg/L]	Hardness	Ca [mg/L]	Mg [mg/L]
0	6.0	-	42.6	0.051 < NG	-	-	-
23	5.4	-	39.3	1.11	-	-	-

The tests show that the zinc quantities discharged by AQUABION® within 23 h lie in the mg range. The higher value of the first test series is to be attributed clearly to the metallic thermometer.

Moreover, no zinc complex was found: the test results showed that the values of the released zinc were identical to the total zinc content.

Tests in the circulation system with the integrated AQUABION® with copper connectors

On the basis of the experience gained during the preliminary examinations, the main tests of the test series were performed as follows:

1) 6 L pure vater from the institute's own pipe was transferred to a glass aquarium, which was located in an external heating bed, and heated to the required temperature.
2) Simultaneously, the required quantity of CaO was added to two 4 litre units of pure water to adjust the hardness of the total batch of hardened pure water through bubbling of CO_2-containing air, and also brought to the required temperature (earlier the CaO was pulverized to a fine powder).
3) On reaching the required temperature, the CaO solution was added to the 6 L pure water and the pump was switched on (the pump delivered approx. 150 L/h).
4) Then the pH value was adjusted by adding NaOH or HCl. A commercial pH electrode was used for the purpose. It was ensured that the thermometer required for pH measurement was dipped only briefly in the test sample, as it also releases zinc. After 10 minutes, the pH setting was cancelled for this reason, even though there was the risk that the achieved pH value did not correspond 100 percent to the setpoint.
5) The basin was covered well with a lid to counter the effect on concentration through vapourization of water.
6) After adjusting the pH-value, an initial sample was extracted, the start parameters were determined and the test phase was started
7) After 1 h and 23 h, samples were extracted and the following parameters were determined. For the 23-hours sample, the remaining volume was determined in advance through calibration and the vapourized water minus the volume of the 2x100 mL sample was filled with pure water.

The zinc determinations with the help of HACH-LANGE cuvette tests – as became conspicuous only later – were disturbed by copper ions over concentrations > 50 mg/L (discharge by the copper pipe and the brass in AQUABION®). In one case after a week, the measurement results differed so blatantnly from the rest that this became conspicuous and the test series was repeated: without this weekend effect, the results matched.

Some observations in detail

- The AQUABION® released between 0.9 and 1.9 mg zinc/L of zinc in the medium during the 23 hour test time, dpending on the test parameters (s. Fig. 7.1-2).
- The zinc released under these test parameters is not complex.
- The conductivity and the water hardness did not change during the tests essentialy (fluctuations in water hardness can be explained with the subsequent releae of CaO particles or through the stripping or release of CO_2).
- Zinc releae at higher water hardnesses (8°dH versus 16°dH) is somewhat higher.
- Zinc release under these test parameters is lower for lower pH-values than for higher pH values (s. Fig. 7.1-3)
- The results indicate a slight decrease in zinc release with increasing test period.
- The hardness does not change under the test conditions during the tests.
- Zinc release increases with the hardness (s. Fig. 7.1-4 and 7.1-5)

After a service life of approx. 6 weeks, the AQUABION® was introduced again
and tested for checking the zinc release at:

pH = 6.0
Hardness = 16 °dH

(s. Tab. 7.1-6 and Fig. 7.1-6). The results show that the hardness had reduced by 1.5 °dH at the very start, while the pH-value remained nearly constant.

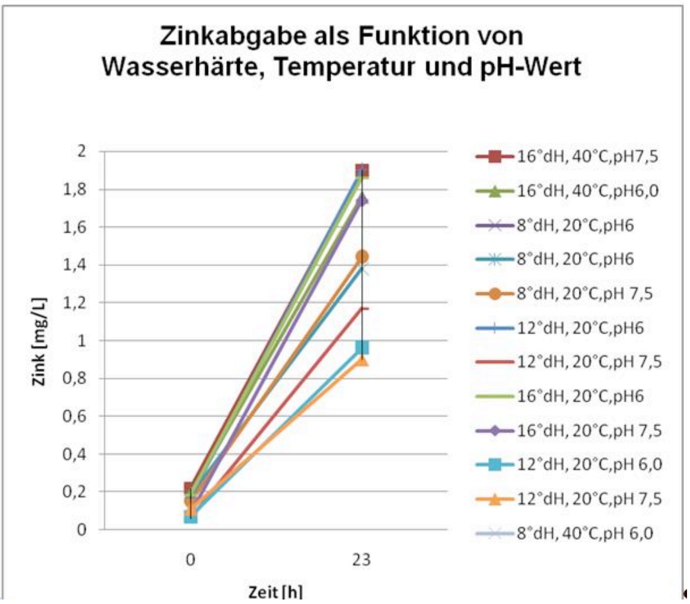


Figure 7.1-2: Zinc release as a function of water hardness, temperature and pH-value

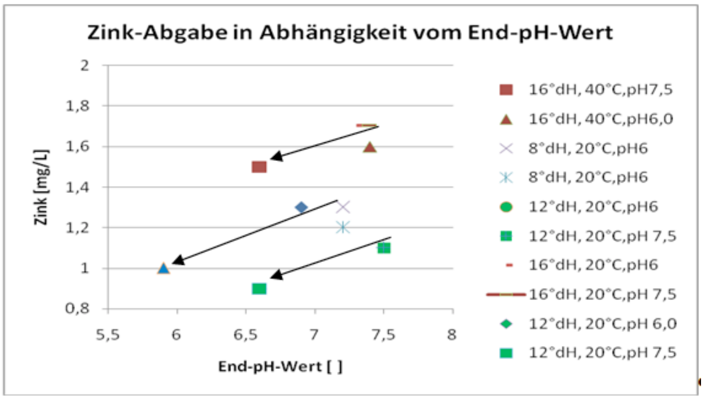


Figure 7.1-3 Zinc release as a function of final pH value [Kunz, P.M., I. Sommer (2008)]

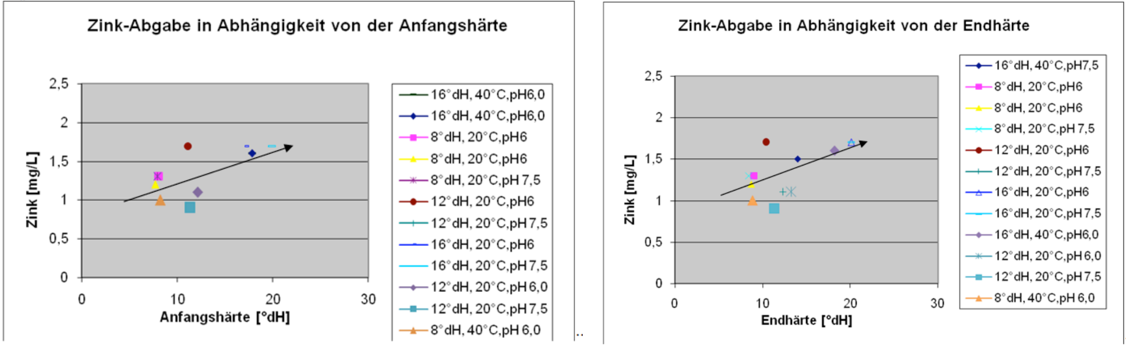


Figure 7.1-4+ 7.1-5 Zinc release as a function of the intitial and final hardness

The change in hardness is presumably conditioned by the problem of full release of CaO (smallest undissolved part can lead to higher findings in the analysis. The zinc release over 11 days was more or less constant and was 0.9 mg/L per day. If one compares this value to previous tests with the same parameters of hardness and pH value, one detects in Figure 7.1-7, that less zinc is released in the medium with increasing duration of the AQUABION®.

Table 7.1-6 Zinc release with use of AQUABION® after long life span (operating duration 11 days, pH 6, 16°dH, 20°C) [Kunz, P.M., I. Sommer (2008)]

Day	pH	Zinc [mg/L]	Hardness	Temp [°C]
0	6.1	0.312	18.3	19.5
1	6.4	1.18	16.8	23.1
3	6.3	2.69	16.6	21
8	6.2	5.58	16.5	21.5
11	6.3	7.11	16.6	23.2

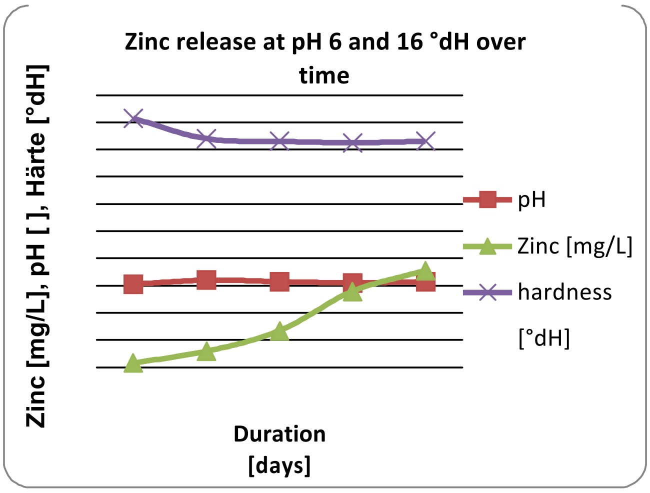


Figure 7.1-6 Course of zinc release and hardness with increasing duration of operation (duration of operation

11 days, pH 6, 16°dH, 20°C) 6 weeks after the first test series [Kunz, P.M., I. Sommer (2008)]

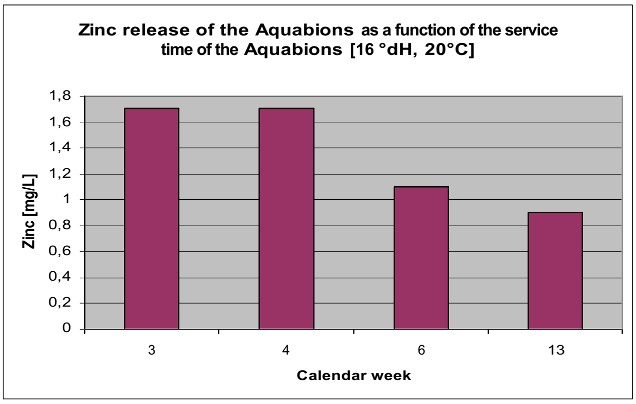


Figure 7.1-7 Zinc release of AQUABION® as a function of the runtime of the AQUABION® [16 °dH, 20°C] [Kunz, P.M., I. Sommer (2008)]

<u>Result from the vapourization of water, which was treated with AQUABION® earlier</u>

- During vapourization of the treated water, there was no lime crust formation on the solid surfaces.

1.5 L of sample 1 with 16°dH, pH 7.5, 20 °C and sample 2 with 16°dH, pH 6.0, 40 °C < are vapourized with the help of two new immersion rods to simulate a heat exchanger.

The following weight increase could be determined for the immersion heaters:

Sample 1: 0.08 g
(20°C)
Sample 2: 0.06 g
(40°C)

Originally 1.6 g CaO/10 L was weighed, i.e., total 0.24 g CaO in each 1.5 L

The results show that very little lime had deposited on the immersion heaters. The biggest part was found on the floor of the glass beaker after the vapourization. It was conspicuous that no lime edges formed on the beaker glass. [Kunz, P.M., I. Sommer (2008)]

Fig. 7.1-8a: Immersion heater

FIg. 7.1-8b: Test arrangement before the vapourization process

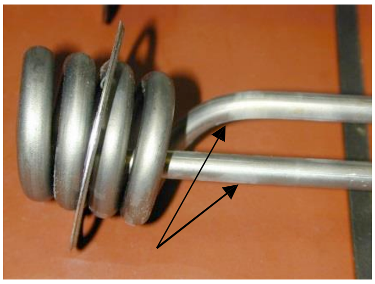


Fig. 7.1-8c: Immersion heater
The vapourization process

Fig. 7.1-8d+e: Lime remains on the floor of the glass beaker [all photos: Kunz, P.M., I. Sommer (2008)]

7.2 LANXESS test results on temperature devices with the AQUABION® [Schulte M., *Function check of galvanic element for water treatment*, LANXESS (o.J)]

On injection moulding devices in practical use (half-a-year) visual comparisons were made of optically blank heating rods. The heating rods with AQUABION® showed less thick coatings, the scratched coatings were optically recognizable as different in quantity and composition (Fig. 7.2-1).

Auswertung
Heizstäbe

Die nächsten Bilder zeigen die Ablagerungsmenge, die bei der Reinigung von 2 Heizstäben abgefallen ist.

Ohne Aquabion

Mit Aquabion

LANXESS

Figures 7.2-1 Deposit quantities after cleaning heater rods [Schulte, M. (o.J.)]

7.3 Test results at Singapore Polytechnic for reduction of the scaling in heat exchangers using AQUABION® [Min, G.WH. and L.C. Yong: Study of Effectiveness of Galvanic Protection on reducing scaling at heat exchangers, Singapore Polytechnic School of Built Environment, Diploma Work (2009)]

The authors found in their water circulation system tests, that without AQUABION® the heater rods were corroded up to 30% versus only 10 % after integration of AQUABION® in the optical comparison (s. optical comparison in Fig. 7.3a and 7.3b).

Fig. 7.3 Heater rods in water circulation systems (a: lef without and b: right with AQUABION®) [Min, Yong (2009)]

7.4 Test results at IWW in cooling water circulation systems for minimizing the biofilm grouth under the use of AQUABION® [IWW Rhineland Westfalia Institute for Water: Report 10275/2009/21100, S. Schulte, (Jan. 2010)]

To check the influence of the AQUABION® active anode system, two rotary piston reactors were used, which were operated in the closed circulation method, based on practical conditions in selected cooling circulation systems at IWW. AQUABION® was implemented in the circulation of one reactor, the second reactor served the purpose of control. In the water phase of the reactor system with AQUABION®, the zinc concentrations were measured. They showed that the active anode system released zinc (in ionic form) over the total test period.

While characterizing the biofilm, it was detected that after 4 weeks, an accumulation of zinc took place in the biofilm from the AQUABION® system. The effect of the AQUABION® influenced mainly the biofilm formation, and less the bacterial concentration in the water phase. It could be shown that the hose which was integrated in the system with AQUABION® was coated much less after 5 weeks than the coat in the hose of the control system. Besides, it was clear that the coating in the hose of the control system had a yellowish-brown discolouration. This makes it absolutely clear that the biofilms in the two systems do not only have different thicknesses, but also different compositions: In the first two test weeks, short bars dominated in both test systems, that were bonded to the coupon surface. From the third test week, there was formation of bacterial aggregates and the occurrence of protozuas could be proven. An essential difference was then the presence of fibrous bacteria only in the control system. With the wetting of the fibrous bacteria, the biofilms that contain them normally enjoy greater stability.

- The cultivation power of the cooling water bacteria in the AQUABION® system was less by a factor of 10 (after a week of test duration, even by a factor of 1000),
- The number of cultivatable legionella specs. In the AQUABION® system was reduced minimum by a factor of 10 after 2 weeks and a factor of 1000 after 5 weeks than in the reference system with AQUABION®,
- A reduction in cultivation power of the biofilm bacteria through zinc ions is thus established. This reduction could also be established in the water phase for the cultivation of legionella spec.

During operation of the two reactor systems, it was conspicuous that in the sample with the AQUABION® more flakes sedimented than in the control reactor. The chemical test of the precipitate showed that the flakes from both test systems have very similar compositions. The calcium concentrations at 56.6 and 56.7 mg/L were equally high (comment: IWW did not differentiate whether the calcium existed in the aragonite or calcite form). A big difference was only in the concentration of zinc in the precipitate: While the presence of zinc in the precipitate from the control reactor could not be proved, the flakes from the AQUABION® contained 14 mg/l of zinc.

8 Balancing thoughts

As mentioned above, the formation of aragonite instead of calcite (slice) **requires only 1 zinc ion**, **to transfer approx. 16,000 carbonate molecules** with the calcium of the water to a mineral which does not form crusts on the heat exchanger surface. The zinc is stoichometrically not involved in the reaction of the aragonite build-up.

It is therefore only of academic interest to consider the extent to which the zinc sacrificial anode gets consumed over the years. Another consideration must be based on whether the "consumed sacrificial anodes are still effective in the sense of task creation, namely aragonite formation instead of calcite build-up. For this more analyses are necessary on the technical centre standard, and especially an evaluation of the following Table 8.1 on the operation parameters.

Test results for weight reduction of AQUABION® [Flettner, M.: *Weight reduction of different AQUABION® systems over several years of use*, personal communications 12.06.2018]

Table 8.1 shows current test results of different AQUABION® models after different use periods, without naming the use conditions (like throughflow, water hardness, pH values etc.).

It is remarkable that only for the model AB H50 after 8 years, approx. 10% of the anodes have dissolved, which means 142 g in absolute terms and 17.75 g/a in relational terms, if one suppresses identical material loss per annum. In model AB S 20, 10 percent material loss was detected only in one case (absolute: 19 g), which means 2.7 g/a relationally. Other aggregates of the same model should be approx. 5%, which corresponds to approx. 1.3 g/a, if one again suppresses material loss per annum. In the AB S15 model it is still lesser: once 9%, corresponding to 0.7 g/a, if one suppresses material loss per annum (else much lesser).

The tests mentioned above have shown that less than 1 mg/L throughflow through the AQUABION® in the initial years after the integration from the zinc sacrificial anode was released; the above mentioned mean data is to be discussed under this aspect, that in the beginning the values were higher and with time (perhaps after 1 or 2 years) they dropped under the mentioned mean values.

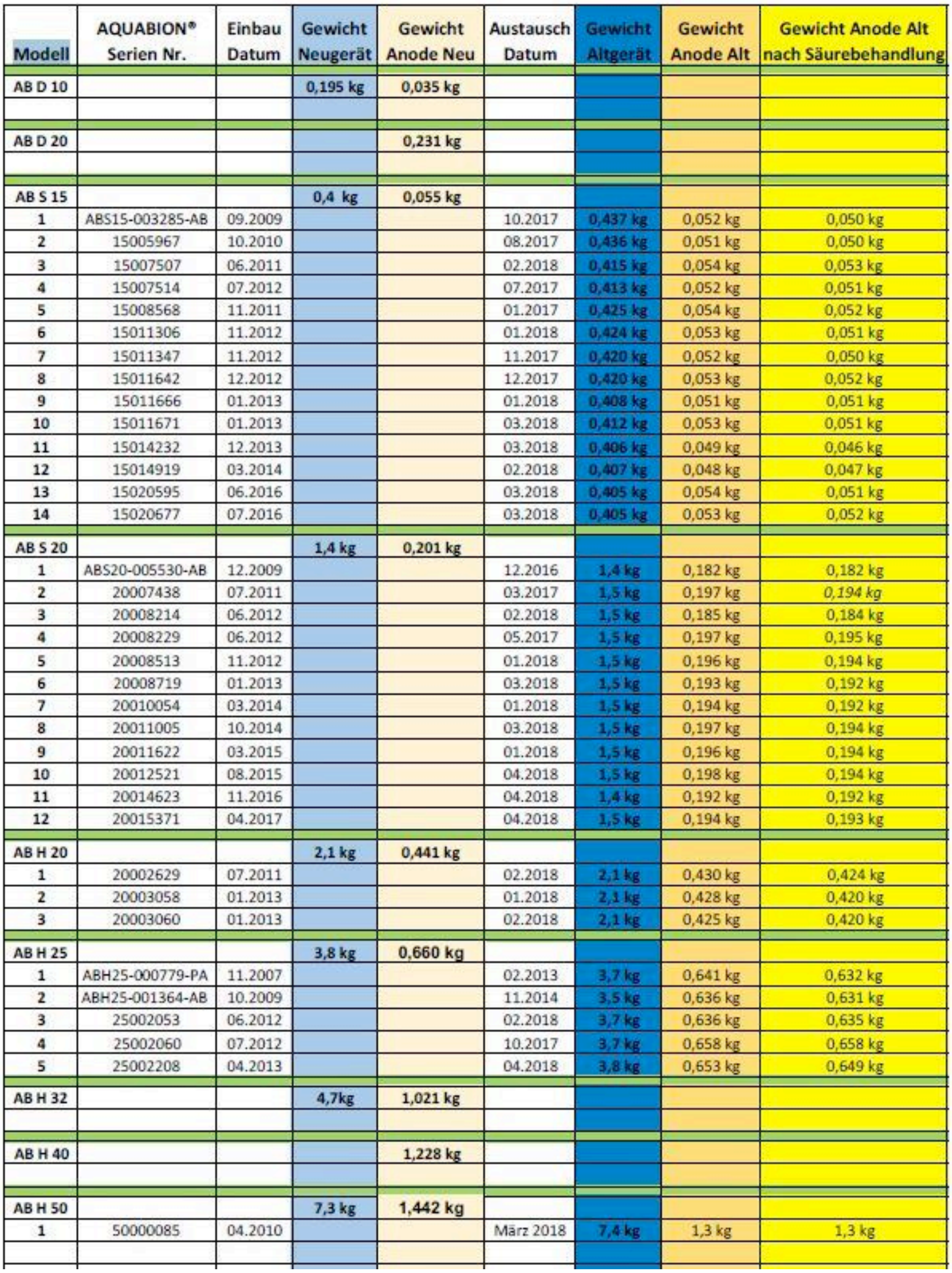
The fact is that after 5 to 7 years 90 % (or more) of the material of the zinc sacrificial anode is still retained.

9 Health aspects of zinc in water, if it is consumed – (WHO and Drinking Water Ordinance)

Zinc is an essential trace element of which the human body contains 2 to 3 gms (as Zn^{2+}); there are predominantly over 300 enzymes, where it is involved in catalytic reactions, and in proteins that stabilizes it [Hasse, H.; L. Rink: *The essential trace element zinc*, Biology time 40, Book 5 (2010)]. The reference values recommended by the German Society for Nutrition for zinc supply to adults is 7 to 10 mg/L (for women or men).

Zinc poisoning is relatively rare, because the required dose for an acute intoxication for men is prevented through vommiting. A (chronic) intake of 25 mg/L is, according to the assessment of the Scienific Committee on Food of the European Commission does not pose any problems [Hasse, H.; L. Rink (2010)].

Table 8.1: Weight loss of different sacrificial anodes in different models at different use times in operation [Flettner, M. personal correspondence (2018)]



Modell	AQUABION® Serien Nr.	Einbau Datum	Gewicht Neugerät	Gewicht Anode Neu	Austausch Datum	Gewicht Altgerät	Gewicht Anode Alt	Gewicht Anode Alt nach Säurebehandlung
AB D 10			**0,195 kg**	**0,035 kg**				
AB D 20				**0,231 kg**				
AB S 15			**0,4 kg**	**0,055 kg**				
1	ABS15-003285-AB	09.2009			10.2017	0,437 kg	0,052 kg	0,050 kg
2	15005967	10.2010			08.2017	0,436 kg	0,051 kg	0,050 kg
3	15007507	06.2011			02.2018	0,415 kg	0,054 kg	0,053 kg
4	15007514	07.2012			07.2017	0,413 kg	0,052 kg	0,051 kg
5	15008568	11.2011			01.2017	0,425 kg	0,054 kg	0,052 kg
6	15011306	11.2012			01.2018	0,424 kg	0,053 kg	0,051 kg
7	15011347	11.2012			11.2017	0,420 kg	0,052 kg	0,050 kg
8	15011642	12.2012			12.2017	0,420 kg	0,053 kg	0,052 kg
9	15011666	01.2013			01.2018	0,408 kg	0,051 kg	0,051 kg
10	15011671	01.2013			03.2018	0,412 kg	0,053 kg	0,051 kg
11	15014232	12.2013			03.2018	0,406 kg	0,049 kg	0,046 kg
12	15014919	03.2014			02.2018	0,407 kg	0,048 kg	0,047 kg
13	15020595	06.2016			03.2018	0,405 kg	0,054 kg	0,051 kg
14	15020677	07.2016			03.2018	0,405 kg	0,053 kg	0,052 kg
AB S 20			**1,4 kg**	**0,201 kg**				
1	ABS20-005530-AB	12.2009			12.2016	1,4 kg	0,182 kg	0,182 kg
2	20007438	07.2011			03.2017	1,5 kg	0,197 kg	*0,194 kg*
3	20008214	06.2012			02.2018	1,5 kg	0,185 kg	0,184 kg
4	20008229	06.2012			05.2017	1,5 kg	0,197 kg	0,195 kg
5	20008513	11.2012			01.2018	1,5 kg	0,196 kg	0,194 kg
6	20008719	01.2013			03.2018	1,5 kg	0,193 kg	0,192 kg
7	20010054	03.2014			01.2018	1,5 kg	0,194 kg	0,192 kg
8	20011005	10.2014			03.2018	1,5 kg	0,197 kg	0,194 kg
9	20011622	03.2015			01.2018	1,5 kg	0,196 kg	0,194 kg
10	20012521	08.2015			04.2018	1,5 kg	0,198 kg	0,194 kg
11	20014623	11.2016			04.2018	1,4 kg	0,192 kg	0,192 kg
12	20015371	04.2017			04.2018	1,5 kg	0,194 kg	0,193 kg
AB H 20			**2,1 kg**	**0,441 kg**				
1	20002629	07.2011			02.2018	2,1 kg	0,430 kg	0,424 kg
2	20003058	01.2013			01.2018	2,1 kg	0,428 kg	0,420 kg
3	20003060	01.2013			02.2018	2,1 kg	0,425 kg	0,420 kg
AB H 25			**3,8 kg**	**0,660 kg**				
1	ABH25-000779-PA	11.2007			02.2013	3,7 kg	0,641 kg	0,632 kg
2	ABH25-001364-AB	10.2009			11.2014	3,5 kg	0,636 kg	0,631 kg
3	25002053	06.2012			02.2018	3,7 kg	0,636 kg	0,635 kg
4	25002060	07.2012			10.2017	3,7 kg	0,658 kg	0,658 kg
5	25002208	04.2013			04.2018	3,8 kg	0,653 kg	0,649 kg
AB H 32			**4,7kg**	**1,021 kg**				
AB H 40				**1,228 kg**				
AB H 50			**7,3 kg**	**1,442 kg**				
1	50000085	04.2010			März 2018	7,4 kg	1,3 kg	1,3 kg

In the large numer of zinc proteins, it is not surprising that nature has found control mechanisms that use buffering systems to compensate for dwindling zinc quantities in uptake through eating and drinking to prevent zinc from creating health problems in people.

WHO guidelines for drinking-water quality

[WHO Library Cataloguing-in-Publication Data: *Guidelines for drinking-water quality* - 4th ed. *(1. Potable water – standards) (2. Water – standards) (3. Water quality – standards) (4. Guidelines)* I. World Health Organization ISBN 978 92 4 154815 1 (NLM classification: WA 675) (2011)] says about zinc: "Zinc is an essential trace element that occurs in nearly all food items and drinking water in the form of salts or organic complexes.

The food is normally the main source of zinc. Although the zinc content in surface water and ground water does not normally exceed 0.01 to 0.05 mg/L, concentrations in piped water can be much higher due to the release of zinc from the pipes.

Reason for not setting up a benchmark: **not health-endangering** at concentrations in drinking water (evaluation year 1993; main reference WHO (2003) zinc in drinking water)

According to later studies on human beings, the derivation of a formal benchmark is still not required at present. Drinking water that contains zinc in quantities greater than **3 mg/L, is however not acceptable to the consumer**.

EU wide defined environmental quality standards – chemical status

[www.umweltbundesamt.de/themen/wasser/gewaesser/fluesse/ueberwachung-bewertung/chemisch#textpart-1]

For chemical status, EU-wide environmental quality standards are defined in the Guideline 2008/105/EG. The EU-wide defined environmental quality standards of the earlier 33 priority substances of the EG- water framework guideline and other eight EU-wide regulated substances of the earlier guideline over the hazardous substances (76/464 guideline, new: 2006/11/EG) determine the chemical status. The rules of the environmental quality standard Guideline 2008/105/EG was accepted by legislators in the Surface Water Ordinance in 2011. The environmental quality standards guideline was amended on 12th August 2013 (2013/39/EU). A total of 45 priority substances was regulated by it, which was taken over in 2016 in die Surface Water Ordinance: **zinc does not figure in it**.

Surface Water Ordinance for the protection of surface water

[Surface Water Ordinance dated 20th June 2016 (BGBl. I S. 1373) replaces V 753-13-3 of 20.7.2011 I 1429 (OGewV)]

The German OGewV [2016] concerns itself with quality standards of water and specifies which substance concentrations display a "good ecological water status". For zinc, the environmental quality standard draws the limit at 800 mg/kg suspended particles or sediment in above ground water on an annual average (Source: BGBl. I 2016, 1410 - 1413).

German Drinking Water Law

The valid TrinkwV [Drinking Water Ordinance (2001) in the version of notification dated 10th March 2016 (BGBl. I S. 459), amended first by Article 2 of the law dated 17th July 2017 (BGBl. I S. 2615) first amended by ordinance on 03.01.2018, see in detail below] **does not contain any data on zinc**. In the TrinkwV from the year 1990, a benchmark was specified for the content of zinc in drinking water (not threshold) of 5 mg/L. This value was not supposed to be exceeded in the pipe after 12-hours of service duration of the water. 2 years after the installation of galvanized steel pipes, the benchmark is valid without considering the service period.

As substance, zinc can he used as a function of the water quality corresponding to the latest technology, **galvanized pipes are allowed in drinking water (cold water regimes)**. [www.ifau.org/trinkwasser/smetalltwinfo-uebersicht.htm].

The objective of the amended drinking water ordinance [TrinkwV (2001)] was to provide drinking water in such a way that its use or enjoyment did not lead to any injury or damage to human beings. Validity area "new" stipulates that the scope of validity does not end at the main shut-off valve, but extends up to the point now where the drinking water is extracted by the consumer (i.e., at the water tap in the kitchen or the hothead in the shower).

Key statement: Drinking water must be procured such that its use or enjoyment does not cause any damage to human health, especially through disease spreaders.

Zinc in drinking water is not regulated in the current German drinking water law – although certain factors must be observerd.

The ordinance on the amendment of drinking water-related legal rules dated 03rd January 2018 converts the Guideline (EU) 2015/1787 of the Commission dated 6th October 2015 for amending Appendices II and III of the Guideline 98/83/EG of the Council on the *quality of water for human consumption* (ABl. L 260 dated 7.10.2015, P. 6) and regulates that the drinking water ordinance [TrinkwV, 2001] in the version of the notification dated 10th March 2016 (BGBl. I P. 459), which was amended first through Article 2 of the law dated 17th July 2017 (BGBl. I S. 2615), has been amended again. The ordinance regulates the quality of water for human consumption, denoted henceforth as drinking water.

§ 3 defines in section 1:"Drinking water" refers to each and every aggregate status of water, irrespective of whether the water is delivered through pipelines, in water transportation vehicles, from drinking water storage tanks in roadways vehices, ships or aircraft, or in closed containers,

a) All water types that in its original condition or after treatment, is meant for drinking, cooking, preparation of food and drinks or especially for the following household purposes:
   - Body care and cleaning,
   - Cleaning of objects which come in proper contact with foodstuff ,
   - Cleaning of objects that come in contact with the human body not just temporarily;

b) All water that is used in a food company for the production, treatment, conservation or marketing of products or substances intended for human consumption.

According to § 11 "List of treatment substances and disinfection methods", reference is made to the 19th amendment to the §11 list which is maintained by the Federal Environment Office [Notification of the list of treatment substances and disinfection methods according to § 11 of the Drinking Water Ordinance – 19th amendment – (version: December 2017)]

During the extraction, treatment and distribution of drinking water, only those treatment substances and only those disinfection methods are to be used which are mentioned in the current list. Exceptions are valid only upon the submission of an approval of the Federal Environment Office under the preconditions of § 12 TrinkwV [2001]. Treatment substances are all substances that are used to extract, treat and distribute drinking water up to the extraction point and through which the composition of the extracted drinking water can change (§ 3 No. 8 TrinkwV [2001]. Only those treatment substances (including their ions as long as these are supplied by ion-exchangers or through electrolysis) can be used, which are necessary to achieve mimimum one of the following treatment objectives:

a. Removal of undesirable substances from raw water through treatment in a water plant.
b. Changing the composition of the water for observing the requirements of the drinking water quality in the distribution network up to the extraction point of the consumer. The requirements can go beyond the requirements of the drinking water ordinance, e.g., with regard to chemical corrosion properties. Change in the composition of the water includes the treatment for technical purposes (e.g., softening).
c. Killing or deactivation of disease spreaders: … (not relevant here)

As AQUABION® does not follow any treatment objectives and is not an electrolysis (to create ozone or similar ROS (reactive oxygen species) – oxygen radicals) in the sense of the ordinance, AQUABION® conforms to drinking water and can be **used in the drinking water area** [Grunert, A. (UBA): Personal communication dated 07.06.2018].

The European rules of standardization series "products for the treatment of water for human consumption" was used as basis for checking the requirements of treatment substances according to § 11 Trink- wV [2001]. This guarantess an international harmonization of the quality of treatment substances for the production of drinking water. The product standards are applicable in their totality for guaranteeing the quality of the treatment substances.

The same method is followed all over Europe, including Sweden:

Livsmedelsverkets föreskrifter om ändring i Livsmedelsverkets föreskrifter (SLVFS 2001:30) om dricksvatten (Specifications fo Danish foodstuff authorities)
beslutade den 21 september 2017. Med stöd av 5, 6, 30 och 31 §§ livsmedelsförordninge

5 § Dricksvatten får inte innehålla några ämnen som används vid beredning eller distribution av dricksvatten, eller föroreningar som harsamband med sådana ämnen, i högre halter än som är nödvändigt för att tillgodose ändamålet med användningen. Dricksvatten får inte heller innehålla material från installationer som används vid beredning eller distribution av dricksvatten, eller ämnen som har samband med sådana material, i högre halter än som är nödvändigt för att tillgodose ändamålet med användningen av materialen.

According to information provided by Johan Eliasson [e-mail dated 19.06.2018]: "This is what the answer we got from the Swedish authorities: *Det finns inga gränsvärden för zinc i dricksvattenföreskrifterna. Även om det saknas gränsvärden, såkan åtgärder krävas om vattnet bedöms utgöra en hälsorisk.* (There are no limit values for zinc in the drinking water regulations. Even if there are no limit values, action may be required if the water is considered to be a health hazard. [Hälsningar, Johan Eliasson, 0451-131 00]." And on 25.06.2018: "It is the same regulation on commercials: *Ja, dricksvattenföreskrifterna gäller även för kommersiella verksamheter (t. ex. restauranger) med egen brunn* [Bo Eliasson, www.aquagruppen.se

For AQUABION® one must also consider the requrements of the DVGW work sheet W 204 "Treatment as well as substances in drinking water provision – rules for selection, procurement and quality assurance ". The use of not listed ion exchangers and other filter materials (e.g., filling bodies,natural sand for slow sand filtration) for treatment of drinking water, which were in operation before the introduction of the list (in December 2017), may continue in accordance with the generally recognized rules of technology and proven effectivity. Here one must ensure that no checmical substances from ion-exchangers or other filter materials make their way into the treated water, which have an avoidable or unacceptable effect on health and the environment.

- **As mentioned above, zinc ion in concentrations below 3 mg/L [WHO] do not pose any threat, which is why there are no thresholds for drinking water all over Europe.**
- **The IWW results cited above (Secition 7.4) show that the AQUABION® stabilizes the hygienic concerns in water and e.g., restricts biofilm formation and has other positive effects concerning the growth of legionella in the water system.**

Hygienic requirements of materials and substances that come in contact with drinking water

The Federal Environment Office defines in the form of legally binding applicable evaluation principles, according to § 17 Section 3 of the TrinkwV 2001, the concrete hygienic requirements of materials and substances that come in contact with drinking water. Earlier, the Federal Environment Office has published guidelines and recommendations on materials and substances that come in contact with drinking water. Hygienic requirements are also formulated in the DVGW regulations (e.g., W 347). These will apply till appropriate legally binding UBA evaluation principles are defined. The hygienic requirements are defined for materials or substances specifically and are listed below.

Metallic substances must be listed in the positive list of metallic substances suitable for drinking water hygiene – the part of the evaluation basis for metallic substances that comes in contact with water. The current positive list contains numerous alloys that contain zinc [http://www.wgm-berlin.de/de/resources/UBA_Positivliste_metallene_Werkstoffe_Stand_2017.pdf vom 22.06.2018].

DIN 1988-200 Technical rules for drinking water installation – Section 200: Type A installation (closed system) – Planning, components, appliances, substances; technical rules of DVGW, May (2012)

General information (in Section 3.4 Substances, components and appliances)

The substances and materials that come in contact with drinking water must be hygienically safe and should not impair the quality of the drinking water defined in TrinkwV [2001]. They should not release substances in concentrations that are higher than absolutely unavoidable qualtities under the generally recognized rules of technology, or that directly or indirectly reduce the protection guaranteed in the TrinkwV [2001] of human health, or that influence the odour or taste of the drinking water.

➔ **Metallic substances must correspond to the requirements of DIN 50930-6.**

According to § 12 (4) of the AVBWasserV [*Ordinance on the general conditions for the provision of water* dated 20th June 1980 (BGBl. I S. 750, 1067), amended first through Article 8 of the ordinance dated 11th December 2014 (BGBl. I S. 2010), amended (2014)] only materials (components and substances) and appliances should be used which have been procured according to the recognized rules of technology. The stamp of a recognized certification authority, e.g., DIN/DVGW or DVGW certification stamp guarantees that these preconditions have been satisfied. Information and criteria for the selection of metallic piping substances giving due consideration to corrosion probability are mentioned additionally in DIN 50930-6. Substances for drinking water installations should be planned and selected such that the use of systems for the treatment of drinking water is not required.

All the system parts coming in proper contact with drinking water can change the quality of the water flowing through them. These changes and enrichments must stay within the limits defined in TrinkwV [2001] and should not exceed them. In addition to the designer and the installing company, the operator of a drinking water installation are responsible for the observation of these thresholds and parameters. The parameters are to be observed at each extraction point in a drinking water installation (remark: food processing company).

Information about the corrosion probability of different substances is available in DIN 50930-6 or the DIN EN 12502 Series. A drinking water treatment such as mechanical filtration protects against particle-induced hole corrosion. A chemical dosing can be used to reduce the corrosion probability, which could otherwise lead to damages.

Exactly when deposits are formed, is difficult to determine. The tendency of the water to separate lime increases with increasing water temperature. If slice build-up is to be expected, a drinking water treatment may be considered (e.g., softening of water through ion-exchange according to 12.6, Dosing of chemicals as per 12.5 or with the help of lime protection devices according to 12.7). Solid particles, irrespective of their nature or their origin, form deposits in the pipes. They can create areas in the pipes that have different amounts of ventilation, in which the metal covered by the deposits work as anodes. Deposits can also favour the multiplication of microorganisms. Both occurrences can cause corrosion which remains undetected and can lead to pipe perforation, see 12.7 Lime protection devices: Lime protection devices work on the principle of seed crystal formation. The protection effect is achieved through microscopically small, undissolved seed crystals produced with the help of the device, on which the hardening agents are deposited during the adjustment of lime-carbonic acid equilibrium. The hardening agents remain in the water. Almost no softening takes place in the lime protection devices. Lime protection devices must correspond to DVGW W 510.

➔ **AQUABION® is not covered by this section, because it does not release any seed crystals (undissolved substances) in the surrounding water definitively, it releases zinc ions instead.**

Lime protection devices reduce the slice formation in the treated water without changing the composition of the drinking water. They protect heating coils, valves, pipe inner walls and other surfaces that come in contact with water from deposits. The size of the lime protection device is based on the expected nominal flow. It is recommended that the lime protection device be installed after a filter, so that dirt particles and sand can be prevented from streaming in.

see 18.2 Cathodic corrosion protection: Methods of cathodic corrosion protection in the drinking water installation are used only for storage and drinking water heaters
(see DIN 4753-10).

➔ **Here it can be stated that "cathodic corrosion protection" is also achieved by AQUABION® in drinking water.**

10 Summarizing core statements - Prospects

Speaking from the technical drinking water view point, AQUABION® is an apparatus which releases zinc ions in the water surrounded by the zinc sacrificial anode on the basis of galvanic elements (without current supply). The AQUABION® differentiates itself from dosing systems which add certain substances to the water (e.g., those that form seed crystals), so that this leads to the release of zinc ions from the sacrificial anode. The released zinc ions lead to the fact that instead of hard slice (calcite) calcium carbonate crystals grow as a result of the vapourization or heating of water, which differ from calcite: In different tests, more than anything else, aragonite was found in spherical or plate type structure, which can be simply extracted or removed without acids.

Zinc is released from the zinc sacrificial anode in larger quantities (concentrations of 0.9 mg/L were found) after the integration of new fittings) – the weight reduction of the sacrificial anodes after 5 years or more or operation however, (Base 34 fittings) is less than10 % or below 2g/a.

This released zinc does not participate in the calcium carbonate build up, neither does it appear in a stoichiometric balance equation: It is reported that a zinc ion in hard water is sufficient to crystallize more than 16.000 calcium carbonate crystals in the aragonite form.

As zinc is essentially meant for human beings (because, among other things, it is used in many enzymes), WHO does not see any reason at present (since 15 years) why it should define a threshold for zinc. For the protection of consumers, WHO has fixed a benchmark of 3 mg/L. Water, even the water that flowed through the AQUABION® during initial operation, can therefore be enjoyed safely. No thresholds have been defined for zinc in European law, especially German and Swedish law on drinking water.

The effect of AQUABION® influences the biofilm build-up in pipes/hoses favourably (less coating and more stable, less strong, less corrosion products as compared to the control system). The number of the legionella spec. that can be cultivated in the AQUABION® system after 2 weeks was reduced by a factor of minimum 10, after 5 weaks of test duration, it was reduced by a factor of 1,000 as compared to the number in the referenc system without AQUABION®. AQUABION® therefore also has hygienically positive aspects for drinking water – especially with regard to legionella (say from shower hotheads).

Peter M. Kunz

Prof. Dr. Peter M. Kunz, 03.07.2018