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Corrosion in Heating and Cooling Water Circuits - A Field Study

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Abstract

Corrosion and clogging are hidden hazards in various engineered systems dealing with water as storage or heat transfer medium. The related efficiency and serviceability losses may entail expensive remedial measures and costs up to the range of millions (€). Especially modern low-exergy installations are affected. They may suffer from oxygen ingress through capillary tubes, higher microbial activity due to moderate temperatures and increased vulnerability of complex components to particulate corrosion products. This field study presents in-situ investigations of chemical and microbial water quality and corrosion in pipes of different non-residential buildings. It identifies processes and recommends measures to prevent corrosion. Causes of corrosion and clogging were found to be i.a. related to operational errors.

Keywords: Corrosion in heating and cooling systems, corrosion monitoring, corrosion prevention, technical building services, microbially influenced corrosion (MIC), quality assurance, asset protection

1. Introduction

Corrosion and scaling processes take place in virtually all systems using water as a thermal fluid [14]. In the building sector, corrosion occurrence and clogging-induced reliability problems have become more prevalent in recent years, often within a time span of 1-2 years after commissioning. Previously, such early effects within the expected service life were seldom. Hence, interest in the topic has been low for decades. Corrosion and prevention in closed loop-systems was regarded as common knowledge on the field of building engineering. The new symptoms are possibly related to a technology mix for thermal conditioning of buildings that meets the target of realizing a nearly climate-neutral building stock" [3].

An exploratory pre-study using an online questionnaire confirmed high actuality of corrosion issues, as 76% of the participants already had experience with corrosion in hydraulic systems and one third states a high or very high risk

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of financial damages. All components (pumps, heat exchanger, heat transfer surfaces, inner and outer pipe surfaces, valves, sensor technology) were believed to be particularly vulnerable to corrosion.

Corrosion is defined as: "*physicochemical interaction between a metal and its environment that results in changes in the properties of the metal, and which may lead to significant impairment of the function of the metal, the environment, or the technical system, of which these form a part*" [4]. Corrosion resistance is not an intrinsic property of the given metal, but a systems property [7]. Eq. 1 shows the basic anodic partial reaction for iron. By further oxidation and precipitation, the soluble metal ions produced by corrosion from particles of insoluble secondary corrosion products.

$$2\,Fe \rightleftharpoons 2\,Fe^{2+} + 4\,e^- \tag{1}$$

The cathodic partial reaction is most often the reduction of H^+-ions (in acid to neutral media) or oxygen (Eq. 2 [12, 10]), which produces hydroxide ions.

$$O_2 + 2\,H^+ + 4\,e^- \rightleftharpoons 2\,OH^- \tag{2}$$

Classical systems used to be mostly oxygen-tight. Initial corrosion on the large steel surfaces (anode) rapidly consumes dissolved oxygen (cathode) from fill-up water or small amounts of make-up water. High temperatures and oxygen-depleted conditions favoured the build-up of the Fe(II/III)-mixed oxide mineral magnetite (γ-Fe_3O_4) which forms black passive layers, protecting the underlying carbon steel. In oxygen-rich environments the rusty-brown pure Fe(III)-minerals goethite (α-FeOOH) and hematite (α-Fe_2O_3) form. In contrast to the tightly-packed spinel conformation of magnetite, these layers leave the metal surface in the active state. Deplenished oxygen concentrations and formation of protective layers inhibit the cathodic reaction 2, preventing dislocation of electrons and thus hindering the primary anodic corrosion reaction 1.

In oxygen-depleted conditions, further oxidation of Fe^{2+} and subsequent hydrolysation of the strong cation-acid Fe^{3+}, producing H^+, is hindered, so that the system alkalises. Alkaline media hinder the cathodic reaction 2 even more. Corrosion rates are minimised to few micrometers per annum or less.

The related negligible particle loads from such slow reaction processes did not affect classical pumps. Besides higher temperatures, higher heating loads generate high flow rates and gaps in the classically smaller number of valves controlling these systems. In contrast, modern energy-efficient buildings and systems are highly automated [1]. Efficient pumps with permanent magnet motors and valves for hydraulics control have smaller gap dimensions by design. These parts are generally more vulnerable to corrosion products. Alongside the heat/cold demand of a room (depending on the quality of the building envelope and the utilisation patterns), the system temperature is a core parameter: it determines size and construction type of the transfer system [3]. Extensive heat transfer surfaces (e.g. capillary tubes for subfloor heating, wall heating or surface cooling systems) facilitate the use of a smaller temperature difference, viz. moderate temperatures, for conditioning [3]. As only few specialised bacteria genera are able to grow at elevated temperatures above 60 °C, microbial corrosion might be more relevant in low-exergy heating and cooling systems. In the present study, we analysed abiotic and biotic corrosion processes. Novel prevention and monitoring strategies were investigated. The scope embraces circuits of different dimensions, materials, temperature levels, water treatment and other operational conditions.

2. Methods

This field study of closed heating and cooling circulation systems consisted of inspection of 64 water circuits in 21 buildings (waterchemical and microbiological laboratory analyses and on-site measurements) and online corrosion monitoring of eight circuits. Among the systems are primary and secondary circuits for heating and cooling i.a. from high-rise office buildings and buildings with retail spaces and fill volumes >10 m^3. The systems differ in materials, operation modes and fill-up waters. Several circuits contain corrosion inhibitors and other water treatment additives. For some cycles, corrosion effects were known prior to analysis. [16]

To assure representativity of point measurements, uninterrupted usual operation of the system for at least 24 hours prior to monitoring and sampling was arranged, as communicated to the building operators. Spigots were fully opened and rinsed before sampling. The on-site parameters redox potential, pH-value, temperature, dissolved oxygen and specific electric conductivity were measured in a flow-through cell using sensors by Hamilton® (EasyFerm Plus ORP Arc 120 Pt, EasyFerm Plus PHI Arc 120, VisiFerm DO Arc 120, Conducell 4 USF Arc 120).

Web-based corrosion monitoring was done as described in Wiegand et al. [16] using the formulas by Opel et al. [13] for ferrous iron activity and ferric iron mineral build-up rate. Alert functions (”traffic lights”) and deeper layers of data analysis such as graphs and background information were visualized on an online dashboard using a building technology management software (Synavision GmbH). The ”traffic lights” assessment scheme is meant to provide non-experts with useful information on the system condition and water-chemical changes leading to clogging. The scheme includes threshold values from German guidelines [5, 15, 2] and adaptations from project experience.

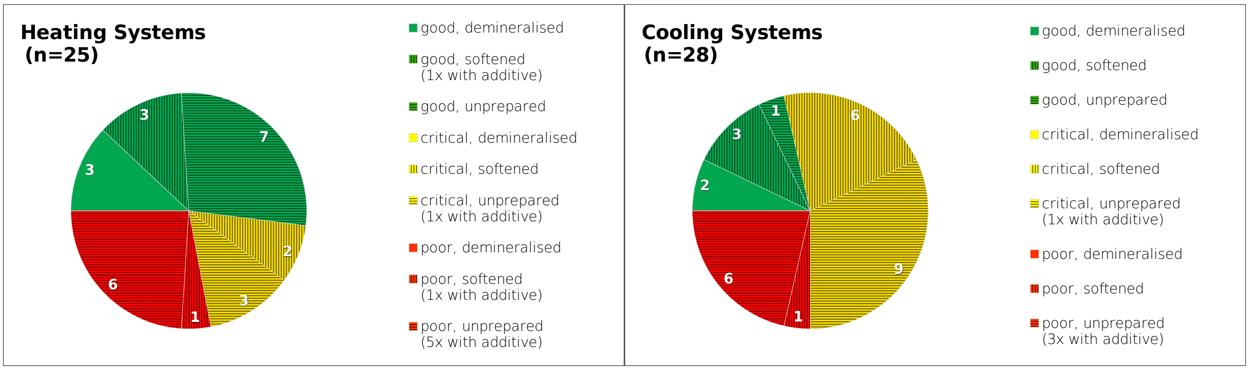
The sensor values were compared to a reference measurement by ICP-OES (Optima 3300RL AS 90 by Perkin Elmer; multi element standard CertiPUR® St. IV by Merck KGaA). Samples were collected into 10-ml polypropylene tubes (Sarstedt AG & Co.) and preserved with HNO_3 (SupraPur, Merck KGaA). Filtering immediately through a 0.2 µm filter (cellulose acetate, Rotilabo® C. Roth GmbH & Co. KG) returns the soluble iron concentration. Nitrate, chloride and sulfate were determined using ion chromatography (Dionex Dx-120). For determination of total organic carbon, samples were collected into clean dry glass bottles and analysed by a TOC-VCPN (Shimadzu Corp.). Determination of organic acids was assigned to an external service provider (Eurofins Umwelt Nord GmbH; in-house method according to PA 1202 (GC-FID)).

For identification of bacterial genera and linked metabolic processes, samples of 800 mL (n = 34) were collected into 1 L sterilized screwcapped PP flasks and directly filled up with 200 mL denatured ethanol using sampling Kits (”Blue BioSeq” by Blue Biolabs, Berlin, Germany). 16S rRNA-analysis and subsequent alignment search using the Basic Local Alignment Search Tool (BLAST) was assigned to an external service provider.

3. Results & Discussion

3.1. General Findings

Non-optimum conditions and corrosion effects were found in several objects, some of which were relatively new or even not yet occupied. Of the 53 systems which were assessed on the basis of dissolved and particulate metals, on-site measurements and anions/organic carbon, 34 systems showed poor or critical conditions (Fig. 1).



(a) Heating systems

(b) Chilled water systems

Fig. 1: Fill water and system condition ‘good’, ‘critical’ and ‘poor’ based on threshold values and project experience.

Some of the identified poorly performing circulation systems contain water additives, some of which dosed to avoid corrosion. Most systems were filled with softened water or untreated tap water, only a small number of systems was filled with demineralised water. All systems with demineralised water showed good conditions. Also a number of cases using softened or untreated tap water were classified as ‘good’. Table 1 shows water constituents in the analysed circuits.

Table 1: Water composition of heating (☼) and chilled water (∗) circuits.

	IC	TOC	Cl^-	NO_3^-	SO_4^{2-}	$Fe_{aq.}$	Fe_{total}	Cu	Mn	Zn
☼	27 ± 30	693 ± 2305	31.0 ± 30.8	0.3 ± 0.5	2.7 ± 9.5	15.2 ± 43.1	20.4 ± 46.1	0.6 ± 1.9	0.4 ± 1.2	0.2 ± 0.5
∗	23 ± 13	98 ± 308	41.4 ± 29.1	0.7 ± 1.9	13.3 ± 27.4	28.3 ± 101.2	31.8 ± 113.6	0.3 ± 0.7	0.2 ± 1.0	0.2 ± 0.5

Mean Values ± StD [mg L^{-1}]

Dissolved oxygen concentrations ranged from 10 to above 100 µg L^{-1}. Concentrations >50 µg L^{-1} were found in n = 7 cases, >100 µg L^{-1} in n = 4 cases. No parameter predicted the occurrence of corrosion alone. pH and conductivity were of highest significance when linearly correlated. Of the water constituents, chloride was the species of highest single importance, known to damage protective magnetite layers [7, 12]. Installations with chloride concentrations below 15 mg L^{-1} in the system water showed no signs of enhanced corrosion, whereas concentrations above 15 mg L^{-1} often showed increased corrosion. Corresponding conductivity measurements showed good system performance up to 250 µS cm^{-1}. However, some were in good conditions nonetheless (Fig. 2). The findings are consistent with the notion in corrosion science that the corrosion behaviour of metals is ”governed by complex interactions involving many parameters manifesting itself in numerous often unanticipated forms” [7]. The worst conditions were found in systems treated with chemicals meant to prevent corrosion.

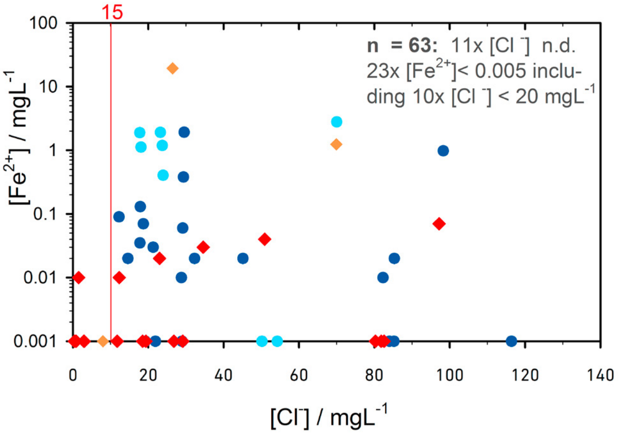


Fig. 2: Cl^- and Fe^{2+} concentrations. Dots: Cooling systems; squares: heating systems; Light colours: pH <8.5; sound colours: pH ≥ 8.5. Note that $[Fe^{2+}]$ were 23 x <0.005 mg L^{-1} with 10 systems with $[Cl^-]$ <20 mg L^{-1}.

3.2. Continuous ferrous iron measurement

Application of the sensor method revealed hidden action in several buildings (undocumented feed-ins, oxygen ingress, loss of system pressure). The sensor signal generally reflects dissolved iron concentrations (Fig. 3, example from a heating circuit). In some cases, the sensor response differed from the laboratory values: Fig. 4 shows monitoring data from a chilled water system of a university building with softened fill water shortly after commissioning. On-site parameters and calculated ferrous iron activity normalised to concentration levels are shown in comparison with soluble iron concentrations. Sudden changes in the on-site parameters starting in the beginning of August lead to an increase in iron concentration reflected by both the laboratory and sensor measurement. In the middle of September, another sudden change detected by pH and redox potential simultaneously with a change in tendency of the conductivity curve was recorded. After the spontaneous decrease in system water quality, acetic and propionic acids were found in the system water (Table 2). Acid producing bacteria, most likely the cause of the change in pH and iron content starting in August, were found abundant shortly after the described incident (Table 3). They may feed on dissolved organic matter, possibly introduced via softened water from a cation exchange resin. A possible explanation for the changed conditions is the feeding-in of make-up water, which could be supported by the increase in system pressure and the redox potential. The second sudden change in September was probably due to connection or disconnection of a system segment. The sensor shows an early ”all clear” before the laboratory values also stabilise at a low level. For the disparities between the sensor and the laboratory values, there may be two explanations: The first is that the

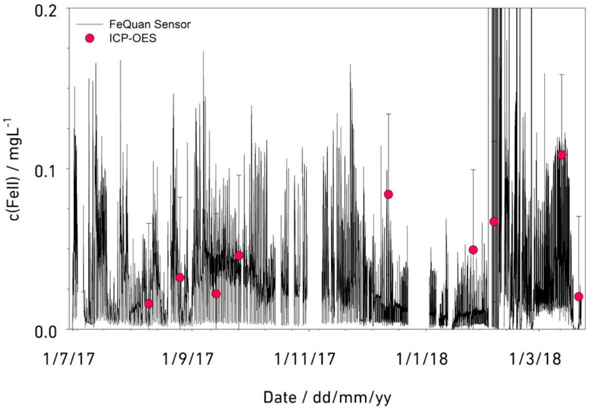


Fig. 3: Continuous ferrous iron-measurement (sensor) in a building heating cycle and laboratory point measurements (red dots).

Table 2: Organic acids and organic carbon [mg L $^{-1}$] in water samples from a chilled water circuit, see Fig. 4 for monitoring data.

Analysis	04/01/18	13/02/18
Acetic acid	110	110
Propionic acid	<50	100
Total organic carbon	44	48

Table 3: Dominant bacteria in a water sample from a chilled water circuit (see Fig. 4 for monitoring data) taken on 13/09/17. The analysis was carried out by 16S rRNA sequencing. Values are the percentage of sequences related closest to the genus stated.

Genus	%	Metabolism
Halomonas spp.	28.13	Anaerobic, heterotrophic, iron reduction
Azospira spp.	16.02	Nitrogen fixation
Novosphingobium spp.	9.36	Decomposition of aromatic matter
Propionibacterium spp.	8.43	Anaerobic, chemoorganotrophic, propionic or acetic acid fermentation
Rhodovarius spp.	4.19	Strictly aerobic thiosulfate reduction, heterotrophic
Acetobacterium spp.	2.50	Anaerobic, acetic acid fermentation

sensor responses are low because Fe(II) is present in complexes with low Fe(II) activity. The second is the presence of compounds which can solubilise Fe(III) from Fe(III) oxides, thus passing the syringe filter, such as electron shuttles or Fe(III)-chelators released by iron reducing bacteria [11] like *Halomonas spp.*

(see Table 3; their capacity to reduce Fe(III) up to elemental iron is described in [6]). Given the later decrease in the laboratory values and the occurrence of *Halomonas*, the latter is more likely. For detection and tracking of corrosion related processes in technical building services, the applied sensor and visualisation turned out to be sensitive tools. Monitoring solves problems arising from lack of information, enabling effective quality management of hydraulic systems.

3.3. Bacterial communities

In the 16S rRNA analyses, approximately 600 different genera were identified. Based on their metabolic capacities, they can be grouped as follows: biofilm formation, oxidation of iron and sulfur, reduction of nitrate, sulfate and iron, nitrogen fixation, acid producing and fermenting bacteria, decomposition of complex and/or halogenated organic compounds.

Biofilms can influence the corrosion of metals (1) by generating corrosive substances (and changing pH) (2) by generating substances that serve as auxiliary cathodic reactants (like polysulfides) (3) by increasing the mass transport of the corrosion reactants and products (4) by consuming oxygen, the cathodic reactant (thus possibly creating reducing micromilieus) [8].

Sulfate reducing and acid producing bacteria might be directly linked to corrosion. *Pseudomonas spp.* genus, a well known slime producer, and fermenting bacteria were found in most systems, completing microbial communities. *Pseudomonas* can use more than 100 different compounds as sole sources of carbon and energy including sugars, lipids, alcohols, phenols, organic acids, and other compounds. [9]

Microorganisms are resistant to many chemicals (antibiotics, disinfectants, etc.) by their ability to degrade them or by being impenetrable to them because of slime, cell wall, or cell membrane characteristics. Resistance may be easily acquired by mutation or acquisition of a plasmid. [9]

The most aggressive MIC takes place in the presence of microbial consortia in which many physiological types of bacteria, including metal-oxidising bacteria, sulfate-reducing bacteria , acid-producing bacteria, and metal-reducing bacteria interact in complex ways within the structure of biofilms [9]

Opel et al. propose an indirect mechanism in which iron oxidising bacteria provide Fe^{3+} (even at low O_2 concentrations) oxidising S^{2-} (produced by SRB) and leading to elemental sulfur nascency at the interface between microaerobic and anaerobic zone. Subsequently, polysulfide forms, acting as another electron acceptor (besides oxygen and the hydronium ion) for the cathodic partial reaction of corrosion. In contrast to the hydrogen and oxygen corrosion, the reaction can take place at elevated pH (Eq. 3). [14]

$$S_{x+1}^{2-} + 2e^{-} \rightleftharpoons S_{x}^{2-} + S^{2-} \qquad (3)$$

The overall process is largely independent from oxygen concentration and pH. Sulfur and sulfide are not consumed. Fig. 5 shows the bacterial community of another chilled water circuit after initial filling of the system and one year later. The composition of the bacterial community has vastly changed by the time

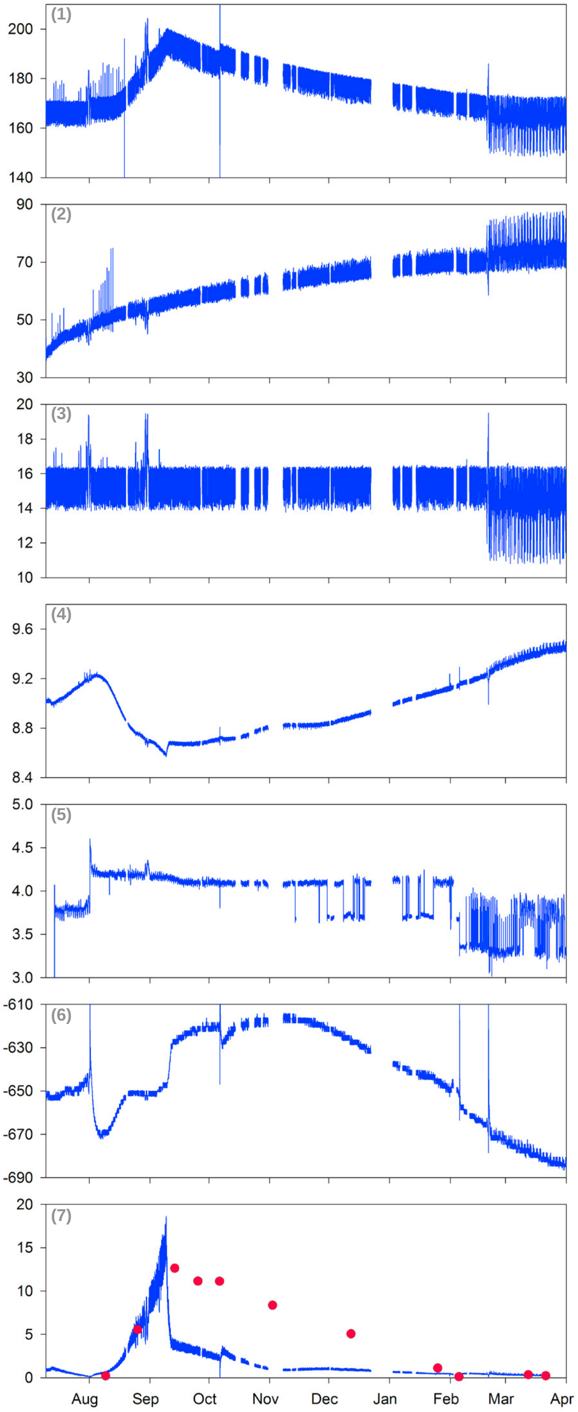
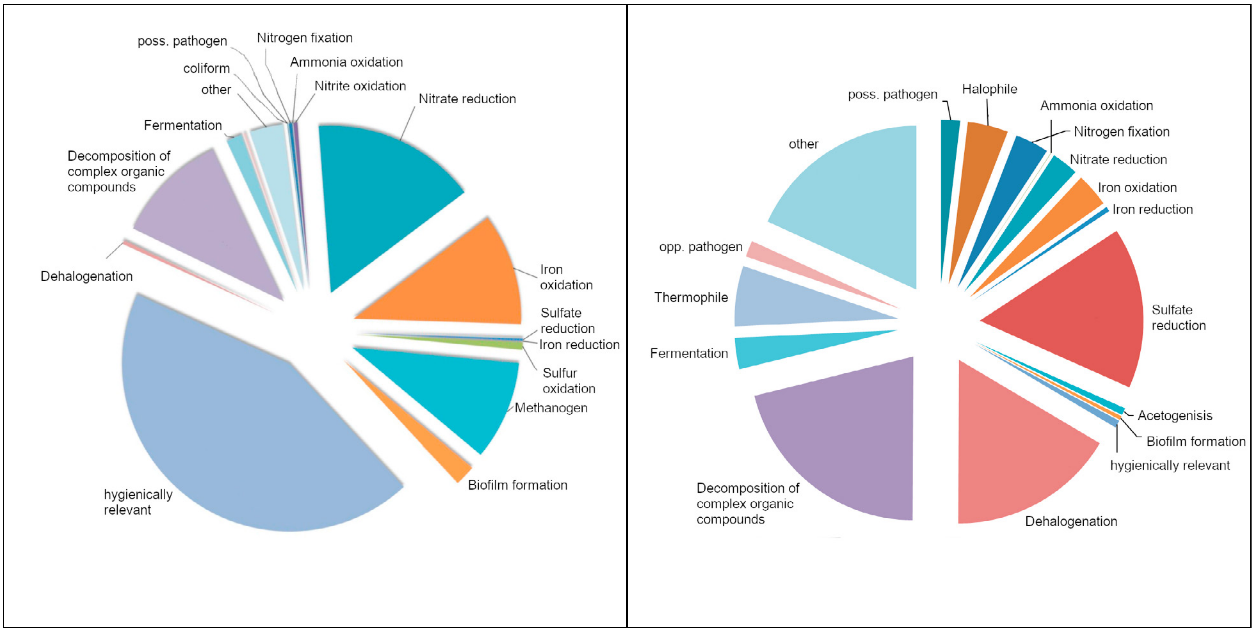


Fig. 4: Data from chilled water circuit. 1-6: Specific electric conductivity [µS cm^{-1}], oxygen [µg L^{-1}], temperature [°C], pH, pressure [bar], redox potential [mV]. 7: Fe^{2+} activity normalized to concentration [mg L^{-1}] from sensor (line) and $Fe_{aq.}$ concentration determined by ICP-OES.



(a) First analysis after commissioning. (b) Second analysis one year after.

Fig. 5: Assessment of the known metabolic capacities of the microbial community in samples from a chilled water system. Some determined bacteria may be included in more than one capacity group. Sequences may originate from living or dead cells.

the second sample was taken. A succession from nitrate reducing, iron oxidising bacteria to sulfate reducing bacteria was observed. Sulfate concentrations decreased from 46 to 0.6 mg L^{-1}. Nitrate was absent in both samples.

4. Conclusion

This study supports the relevance of corrosion prevalent in the building sector. Although low oxygen concentrations are highly desirable, they did not prevent corrosion occurrence in many systems, which might be attributed to MIC. Active bacteria were present in all analysed systems. Our data suggests the use of demineralised water instead of softened water to avoid corrosion. Both, chloride and sulfate, are known to promote abiotic and biotic corrosion. If chloride concentrations are low, usage of untreated tap water is possible. Otherwise, tap water can be blended with demineralised water until attainment of an appropriate water quality. Besides chloride and sulfate, avoidance of elevated organic carbon is a major aim due to promotion of bacterial growth. Organic carbon might be introduced from cation or mixed-bed ion exchangers with ion-exchange resins. Demineralised water from reverse osmosis might be better suited. Apart from state-of-the-art pressure retention, these measures should be valued over the possible use of inhibitors and biocides. Water additives are costly and require additional regular checks during system operation to maintain appropriate dosing. Continuous water quality monitoring can help secure functionality and operational efficiency of heating and cooling systems and reveal hidden actions. Current research of the authors focuses on microbial consortia in engineered systems and different succession pathways.

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