Article

Corrosion Control in Drinking Water Distribution Using Simple Methods

Part 6: Experiments to Determine the Corrosion Rate and Copper Release

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Abstract: Corrosion of copper or copper alloys affects the durability of drinking water installations and the quality of drinking water in associated pipes. This article presents various methods for investigating this issue from different angles. First, it describes a simplified flow-through method for determining copper loss in flowing water, which allows one to determine the corrosion rate, material removal rate, and rate of protective layer formation. Additionally, a testing procedure using a standardized test rig according to EN 15664-1 is presented for evaluating the suitability of copper pipes and copper alloy fittings for a local drinking water. Though labor-intensive, this procedure yields important information about the suitability of copper and copper alloys in contact with drinking water. The test is intended for corrosion-prone metallic materials within regulatory approval processes and cases of uncertainty regarding materials' suitability for specific local drinking water. A third method, a comparable simplified procedure using a closed-loop system, is presented to evaluate behavior under stagnation conditions. In this method, a copper pipe is supplied with water continuously and tested weekly under stagnation conditions to determine the rate of copper release. Both simplified procedures can be conducted in a laboratory with minimal personnel and cost and provide valuable insights into copper corrosion and the release of copper into drinking water.

Keywords: Closed-loop apparatus, copper corrosion, copper release, copper removal rate, corrosion rate, oxygen corrosion, scale formation rate, stagnation test, surface corrosion.

1. Application for copper in drinking water installations

Copper and copper alloys, such as brass, are popular materials for use in drinking water installations due to their excellent workability and low susceptibility to corrosion. Although copper is considered a noble metal, it is not stable in oxygenated drinking water and corrodes. The resulting surface corrosion leads to the formation of deposits (scales) and causes copper to be continuously released into the contact water. The parameter value of 2.0 mg/L, in accordance with Directive (EU) 2020/218 on the quality of water intended for human consumption (DWD), as well as the corresponding parameter value in the German Drinking Water Ordinance, should not be exceeded after 16 weeks of operation [1]. The materials that can be used in drinking water installations and the water-side conditions that must apply are specified in the " Evaluation criteria for metallic materials in contact with drinking water" published by the German Federal Environment Agency (UBA).

https://doi.org/ 10.5281/zenodo.21261812

For drinking water pipes, high-purity, low-oxygen copper with a purity of ≥ 99.90% is required. Furthermore, the following **requirements apply to the drinking water itself: a pH value of ≥ 7.4 or 7.0 ≤ pH < 7.4, and a total organic carbon (TOC) value of ≤ 1.5 mg/L.** This area of application was based on an empirical study conducted by German water suppliers.

The norm EN 12502-2 [2] lists the following factors that influence the probability of surface corrosion of copper in drinking water:

- **the concentrations of carbonic acid species (carbon dioxide, hydrogen carbonate, and carbonate), which can be measured as the total inorganic carbon (TIC),**
- **the duration of stagnation,**
- **the operating conditions,**
- **and the age of the installation.**

This suggests that the TIC (total inorganic carbon) and the pH value, which determines the concentrations of carbonic acid species, are the corrosion-determining parameters for copper. Uniform corrosion in water is considered low when the pH value is above 7.5 and the hydrogen carbonate concentration exceeds 1.0 mmol/L.

According to the DWD, drinking water must have a pH value of ≥ 6.5 und ≤ 9.5, and it should not be aggressive or corrosive. There is no obligation for water suppliers to specify suitable pipe materials. In Germany, drinking water must have a calcite dissolution capacity of less than 5 mg/L, as calculated according to DIN 38404-10. Water suppliers should provide consumers with test results according to EN 12502-1 that enable them to select appropriate materials. Water suppliers are advised to investigate the corrosion behavior of copper because they may be liable for any damage that occurs. The UBA's metal evaluation criteria [4] also states that when selecting materials, specific test results on copper release for a particular supply area must be considered, if available. The supplier would also have to make this data available.

2. Corrosion tests on copper materials

A distinction is made between internal and external corrosion. Internal corrosion is caused by the metal, for example copper, coming into contact with drinking water containing salt and oxygen. External corrosion results from the effects of the respective environmental conditions (air, moisture, soil, building materials, and pollutants) on the outside of the pipe. In drinking water installations, only internal corrosion is usually relevant. However, unfavorable external conditions for copper pipes exist in cases of increased humidity and direct contact with gypsum materials, as these have a corrosive effect due to their high sulfate content. In these cases, the copper pipes must be protected from contact.

2.1. Tests according to applicable standards

There are various standards for testing copper pipes for drinking water installations that reflect the current state of the art and are constantly being expanded and updated. Seamless round copper pipes are suitable for water and gas pipes in sanitary and heating systems in accordance with EN 1057 [5]. In Germany, DVGW worksheet GW 392 [6] must also be complied with when copper and copper alloys are used in drinking water installations. The testing procedures relate to material analysis by the manufacturers, the determination of mechanical properties (tensile testing, hardness testing, bend testing, etc.), as well as the determination of carbon content and the carbon layer test.

In addition to copper, its important alloys, brass, red brass, and bronze are also widely used in drinking water installations. Fittings, meter housings, check valves, and pump impellers are often manufactured of brass or bronze, while reducers and fittings are made of red brass. For metal ingots and castings, they are normed in EN 1982 [7]. In the case of brass, a copper-zinc alloy, dezincification is the most important type of corrosion and the test is carried out using the test rig to be discussed in accordance with

EN 15664-1 [8] in conjunction with exposure in accordance with EN ISO 6509-1 [9]. For passive materials, such as stainless steels, there are other test methods, for example, electrochemical testing in accordance with EN 16056 [10].

European Standard EN 15664-1 [8] describes a test rig procedure for evaluating metal release. According to the UBA's metal assessment criteria, this standard is the reference method for determining metal release for all metals and metal alloys that form a protective layer [4]. According to EN 15664-2 [11], the suitability of a metal or alloy for use in sanitary installations can be demonstrated through tests using three reference waters; this is of particular importance for material manufacturers. On the other hand, the suitability of local water can be tested with certified commercial materials, which is of interest to water suppliers and consumers. The application of this rig test according to EN 15664-1 is described in Chapter 4.

2.2. Further tests on copper materials

In addition to the complex standard procedure, simple tests in flow-through or closed-loop apparatus also provide meaningful data for evaluating the suitability of materials with a specific water [12]. A corresponding test for determining the corrosion rate, copper release rate, and scale formation rate during long-term exposure by examining water-exposed copper segments in a flow-through apparatus is presented in Chapter 3. The measurement of short-term copper release in a recirculation apparatus is described in Chapter 5. Three drinking waters were used instead of the test waters specified in EN 15664-2 in order to evaluate their practical suitability for use with certified copper materials.

3. Simplified test for determining the corrosion rate of copper pipe segments [12,13]

3.1 Experiment description

The corrosion rate can be determined by the weight loss of copper segments that were continuously exposed to the test water in flow-through apparatus [12,13]. The experiment should be carried out over a period of at least several months in order to achieve a stable corrosion rate. Conditions such as flow rate and temperature should be kept as constant as possible, as these influence the corrosion process. Depending on the issue at hand, a number of pipe segments made of the same material are produced, weighed, and exposed together in the water to be tested. At specific intervals, individual segments are removed and weighed, with the weight consisting of the copper and the insoluble scales. This scale consists of corrosion products and solids that have precipitated from the water. It can be selectively removed by etching. Either a two-step process with ammonia solution and hydrochloric acid [14] or the one-step etching with EDTA [15]. In the two-step process, copper(II) compounds are dissolved by ammonia solution, while hydrochloric acid dissolves copper(I) oxide. The corrosion rate can be determined from the weight loss of the etched segment and the length of the exposure interval. The analytically measured copper concentrations in the etching solutions can be used to evaluate the average removal rate, the scale formation rate, and the copper content in the scale.

3.2. Test setup

Three flow apparatuses were set up. Each consisted of a 40-cm-long, 35-mm-inner-diameter vertical plastic cylinder fitted with flanges at the top and bottom. These could be sealed with lids that had integrated inlet and outlet ports. The water inlet was located at the bottom, and the outlet at the top. The effluent flowed through a downstream test pipe for stagnation tests (see Chapter 5), a flow meter, and a water meter (Figure 1).

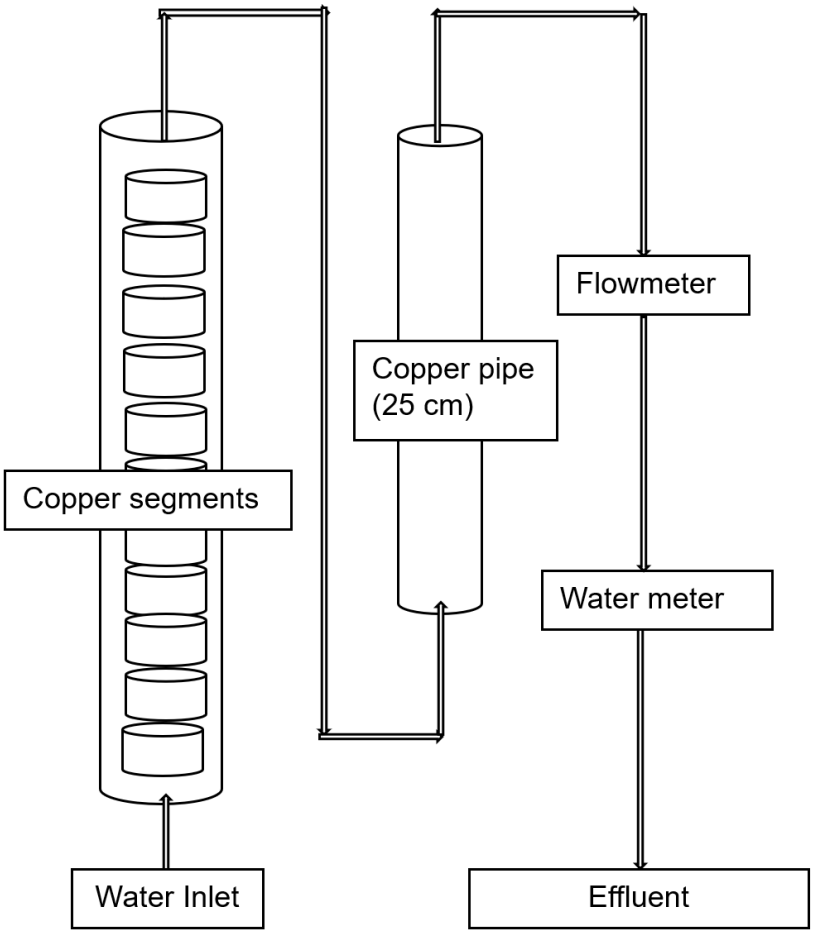


Figure 1. Schematic diagram of the apparatus for continuous exposing pipe segments.

The three identical test devices were continuously fed with different types of water. To prevent algae growth, the devices were protected by opaque covers. The room was temperature-controlled. The inflow was continuously monitored by three Liquisys M CPM253 transmitters from Endress+Hauser Messtechnik GmbH + Co. KG, Hannover, Düsseldorf. Sensors for measuring oxygen content (OXYMAX W COS61), electrical conductivity (Condumax W CLS21), and pH (Memosens CPS11E) were connected to these transmitters. Temperature was available for all sensors. Oxygen was determined according to ISO 17289 [16], electrical conductivity (E.C.) according to EN 27888 [17], pH according to EN ISO 10523 [18], and temperature according to DIN 38404-4 [19].

The XS 204 Delta Range analytical balance, accuracy: 0.1 mg, from Mettler Toledo was used for weight determination.

Elemental analysis was performed in accordance with EN ISO 17294-2 [20] using an Agilent 7900 ICP-MS and MassHunter 4.2 software (Agilent Technologies Germany GmbH & Co., Waldbronn, Germany).

The three test waters originated from the same source of raw water but were treated using different processes. Water 1 was treated with - and activated carbon filtration. Water 2 was treated with natural processes only, including aeration, deep-bed filtration, and activated carbon filtration. Water 3 was partially demineralized by mixing Water 1 with 40% permeate from a reverse osmosis system, followed by aeration. The mean values of the water parameters are listed in Table 1.

Table 1. Mean parameter values of the test waters.

Parameter	Water 1 (oxidatively treated)	Water 2 (naturally treated)	Water 3 (partially demineralized)
Temperature (°C)	14.8	14.9	15.1
pH value	7.43	7.47	7.43
Oxygen (mg/L)	8.0	6.8	8.7
Electrical conductivity at 25°C (µS/cm)	739	720	534
Acid capacity up to pH 4.3 (mmol/L)	3.38	3.47	2.53
Base capacity up to pH 8.2 (mmol/L)	0.30	0.30	0.20
Total hardness (mg/L)	14.9	15.1	10.8
TOC (mg/L)	0.39	0.49	0.35
TIC (mmol/L)	44.2	45.2	32.8
Calcium (mg/L)	86.4	88.2	63.1
Magnesium (mg/L)	12.0	12.1	8.7
Sodium (mg/L)	44.9	44.4	33.5
Potassium (mg/L)	4.51	4.43	3.38
Calcite dissolution capacity (mg/L)	> 0	> 0	> 0
Bicarbonate, calculated (mg/L)	206	212	155
Chloride (mg/L)	83.4	81.8	57.9
Nitrate (mg/L)	12.3	13.4	10.2
Sulfate (mg/L)	53.9	55.3	38.7
Phosphate (mg/L)	0.09	0.10	0.34
Silica acid (mg/L)	8.8	9.1	6.6

3.3. Test procedure

Thirty copper segments were cut from a seamless copper pipe made of Cu-DHP (EN 1057, semi-hard, from KME – Sanco R250). Each segment was 17 to 20 mm high, with an inner diameter of 26 mm and an outer diameter of 28 mm. They were then deburred, cleaned with pentane, dried, and weighed on an analytical balance accurate to 0.1 mg. They were then stacked ten at a time in plexiglass columns. After closing the flange, the apparatus was flushed with respective water at a flow rate of 130-140 l/d for 207 days without pressure, whereby the segments were subjected to turbulent flow from the inside and outside. During the experiment, the average water temperature was (15 ± 1) °C. At pre-determined intervals, a copper segment was removed from each test column, air-dried at room temperature for 24 hours, weighed, and the weight loss after exposure was determined. The last two coupons were sampled simultaneously as quality control specimens.

After removing all segments, the scales were dissolved (etched) separately, the segments dried, and weighed. For this, they were first treated individually for 7 minutes with 15 ml of 25% ammonia solution and then rinsed with deionized water. The etching solution was combined with the rinsing solution, acidified with hydrochloric acid, and filled up to 200 ml in a volumetric flask. In the second step, the segments were treated with 15 ml of 32% hydrochloric acid for 6 minutes and then rinsed with deionized water. The etching and rinsing solutions were combined and filled to 200 ml in the measuring flask. The copper content of both solutions was determined in accordance with EN ISO 17294-2 [20]. The etched copper segments were dried and weighed to determine the copper removal.

3.4. Results and interpretation

After 32 days, the segments, which were bare at the start, were visually covered with a reddish-brown layer, which presumably consisted of copper(I) oxide (Figure 2). From the 81th day onwards, light blue deposits, originating from copper(II) compounds, dominated in Water 1 and Water 2. From the 138th day onwards, the segments from softened Water 3 showed an uneven surface with streaky deposits in the direction of flow. Weight determination after the exposure phase revealed a weight loss for each segment. This demonstrates that the release of copper into the water was a significant process. To determine the corrosion rate, the scale must be removed, as it may contain not only the corroded copper but also reactants such as oxygen and carbon, as well as minerals precipitated from the water—such as calcite or humic substances.

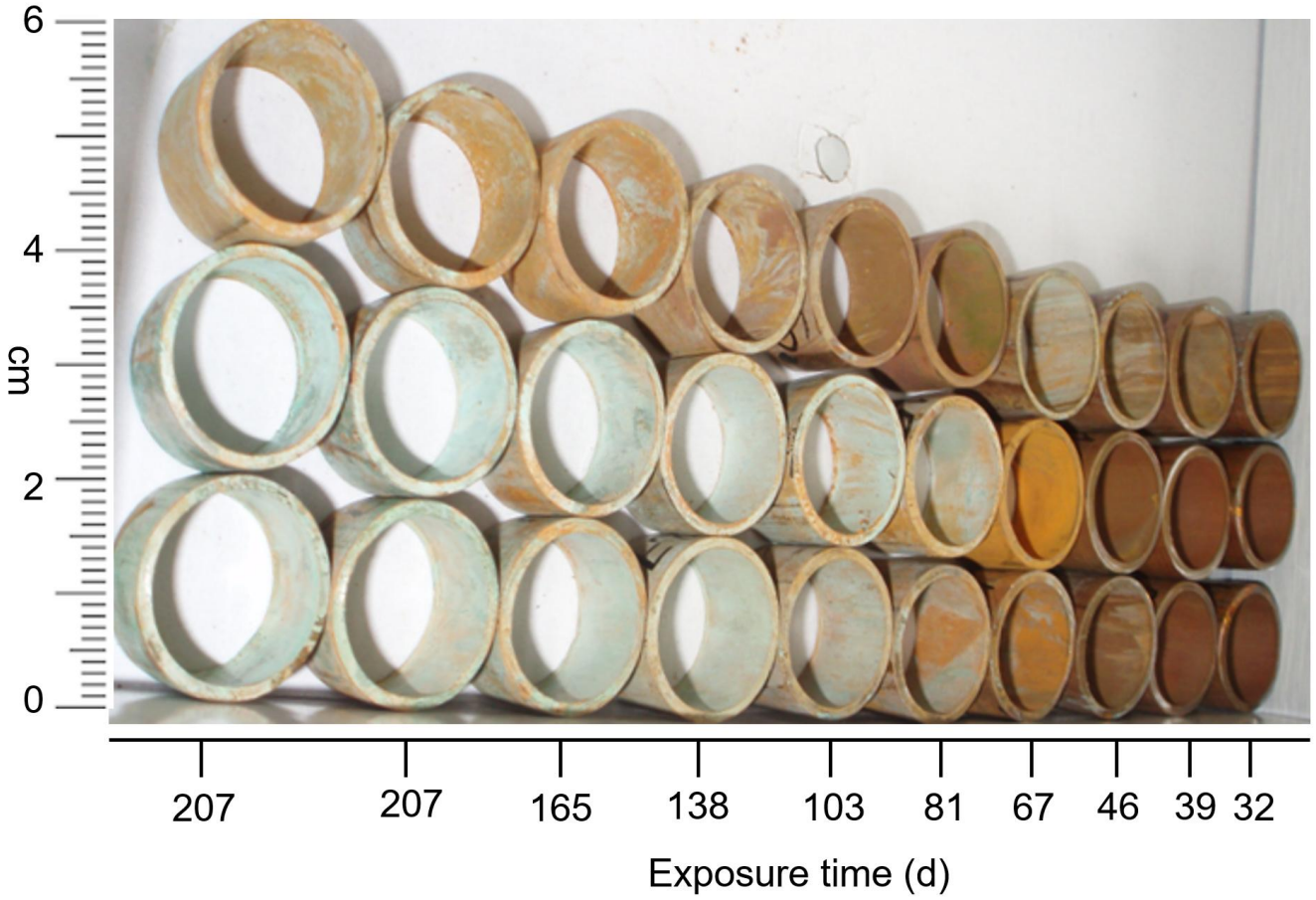


Figure 2. Corroded copper segments after exposure in Water 1, 2 and 3 (from bottom to top).

The copper mass lost due to corrosion is therefore calculated as the difference between the initial weight of the segment and the weight after corrosion and removal of the scale by etching (Equation 1). To determine the copper weight in the scale, the copper content of the etching solutions was determined and multiplied by the volumes of the etching solutions according to Equation 2.

$$\text{Weight loss}_{\text{copper, segment}}\,(g) = \text{Weight}_{\text{segment, start}}\,(g) - \text{Weight}_{\text{segment, etched}}\,(g) \quad (1)$$

$$\text{Weight Cu}_{\text{scale, segment}}\,(g) = \text{Concentration Cu etching solution}\,(g/L) \times \text{Volume solution}\,(L) \quad (2)$$

$$\text{Weight scale, segment}\,(g) = \text{Weight}_{\text{segment, after exposure}}\,(g) - \text{Weight}_{\text{segment, etched}}\,(g) \quad (3)$$

$$\text{Cu removal}_{\text{segment}}\,(g) = \text{Weight}_{\text{segment, start}}\,(g) - \text{Weight of copper}_{\text{scale, segment}}\,(g) \quad (4)$$

$$\text{Corrosion rate } (g/(m^2 \times d)) = \text{Weight loss}_{\text{copper, segment}} (g) / (\text{area}_{\text{segment}} (m^2) \times \text{exposure time } (d)) \quad (5)$$

$$\text{Cu removal rate } (g/(m^2 \times d)) = \text{Cu removal}_{\text{segment}} (g) / (\text{area}_{\text{segment}} (m^2) \times \text{exposure time } (d)) \quad (6)$$

$$\text{Cu scale formation rate } (g/(m^2 \times d)) = \text{Cu}_{\text{scale, segment}} (g) / (\text{area}_{\text{segment}} (m^2) \times \text{exposure time } (d)) \quad (7)$$

$$\text{Cu in the scale } (\%) = (\text{weight of Cu}_{\text{scale, segment}} (g) / \text{weight}_{\text{scale, segment}} (g)) \times 100 \quad (8)$$

The weight of the scale per segment can be calculated as the difference between the weights after exposure and etching according to Equation 3. The copper removal, i.e., the copper carried away with the water, is calculated from the difference between the weights of the segment at the start and that of the copper in the scale according to Equation 4. To determine the corrosion rate, the copper weight loss of the segments is normalized to the respective segment surface area and exposure duration (Equation 5), noting that the coupons were exposed both internally and externally. The removal rate (Equation 6) and the scale formation rate (Equation 7) are calculated accordingly. The weight proportion of copper in the scale is determined according to Equation 8. Substances and processes involved in the corrosion of a copper segment are illustrated in Figure 3.

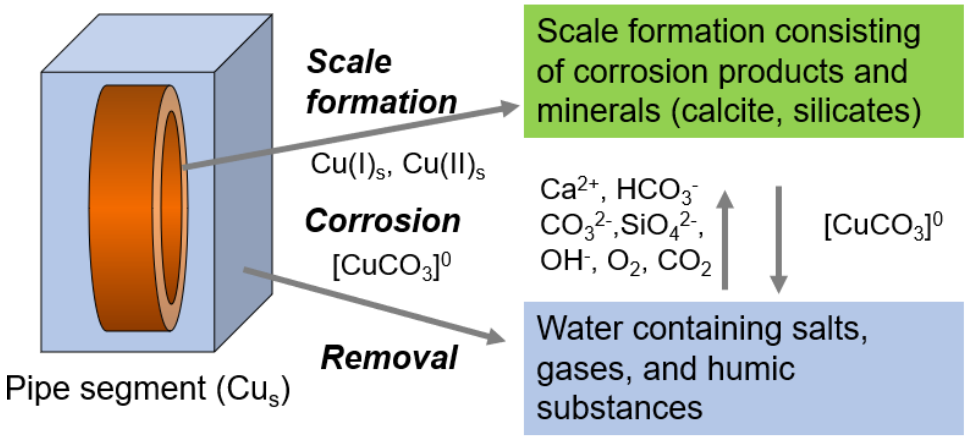
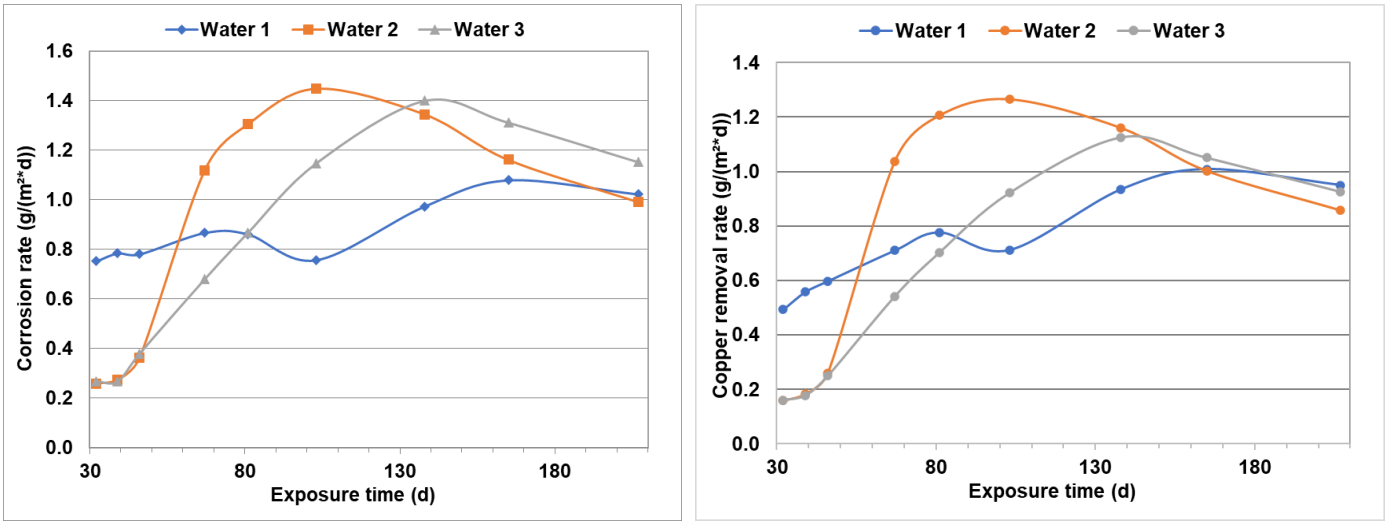


Figure 3. Diagram of the corrosion of a copper segment in water with the relevant species and processes involved, (s: solid).

The differences in corrosion rates between the last two coupons were 4.0% for Water 1, 0.1% for Water 2, and 2.4% for Water 3. These differences can be explained solely by the varying surface areas resulting from the height differences of the coupons, which can be up to 4.0%, demonstrating the reproducibility of the corrosion rate determination.

The investigations revealed corrosion rates in the three test waters that were water-specific and changed over time (see Figure 4a). Even after 207 days (~30 weeks), stable corrosion rates had not yet been reached; however, the curves converged towards the end of the exposure period and ranged from 0.99 to 1.15 g/(m²×d). Thus, the influence of the different treatment methods on the corrosion process decreased with increasing exposure time. These values are within the range of known corrosion constants of 0.68 to 1.86 g/(m²×d) [16]. For fresh and drinking water, further values in the range of 0.12 to 0.61 g/(m²×d) have been reported [17]. Since the corrosion rates of drinking water vary considerably, particularly with regard to hardness parameters and pH value, published data only serve as indicators. **A corrosion rate of 1 g/(m²×d) for copper corresponds to a material loss of approximately 0.04 mm per year.** At the determined corrosion rates, copper pipes would lose 0.8 to 1 millimeters of material thickness within 20 years, which is their overall thickness. However, the graphs suggest that corrosion rates will continue to decrease.



a) (b)

Figure 4. Temporal development of **(a)** corrosion rates and **(b)** copper removal rates of three waters.

The copper removal rates corresponded to the corrosion rates over time, but were slightly lower because copper bound in the scale was not taken into account (Figure 4b).

However, the scale formation rates for copper showed different behavior (see Figure 5). For oxidatively treated Water 1, the coating formation rate decreased from a high level until day 138, increased slightly, and plateaued. In contrast, the scale formation rates of Water 2 (naturally treated) and Water 3 (partially demineralized) did not begin to rise until day 67. They reached their respective maximums after 103 and 138 days, then fell slightly again without reaching a final state.

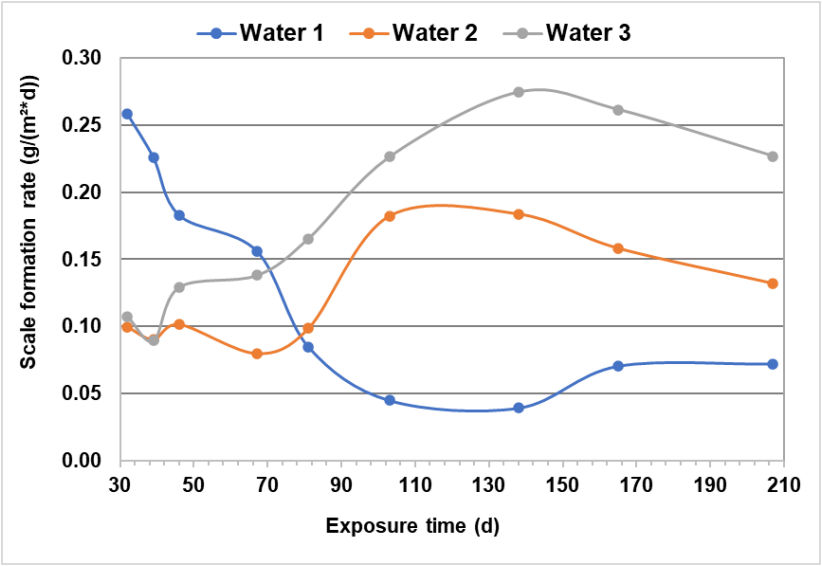


Figure 5. Temporal development of the scale formation rates in the test waters.

The scale formation rates were lower than the copper removal rates. For Water 1, the scale formation rate decreased from 34% to 7% over time. For Water 2, the scale formation rate decreased from 39% to 13%. For Water 3, the scale formation rate decreased from 40% to 20%. These results demonstrate that scale formation is a minor process and that most

of the copper leaches into the water. The increasing dominance of copper removal suggests that a passivating surface layer is not forming.

The proportion of copper in the scale can be calculated using Equation 8 and is listed in Table 2 for the three waters.

Table 2. Temporal variation of the copper proportions in the scale.

	Copper in %		
Exposition (d)	**Water 1**	**Water 2**	**Water 3**
32	32.7	37.3	39.0
39	27.7	31.8	32.6
46	22.4	26.7	33.0
67	17.4	6.9	19.6
81	9.4	7.3	18.3
103	5.7	12.1	19.0
138	3.9	13.2	18.8
165	6.3	13.1	19.2
207	6.8	12.3	18.9

As expected, the copper content in the scale decreased with increasing exposure time, as copper(II) compounds with a lower copper content were formed in addition to copper(I) oxide, and precipitation of calcium carbonate and silicates. If copper(I) oxide were the only component of the scale, the molar weight quotient would result in a copper content of 44.4%. However, this was not achieved for the initial segments. By the end of the exposure period, the Water 3 segment had the highest copper(I) oxide content. This corresponds to the reddish color of the scale in Figure 1. **The experiments showed that the copper(I) content increases as the salinity of the water decreases and subsequently drops again as the exposure time increases.**

3.5. Summary

The test described provides comprehensive data on copper corrosion with minimal personnel and material resources. The corrosion tests on pipe segments, which are carried out over a period of several months, can be used to determine the corrosion rate, the removal rate, and the scale formation rate. The ratio indicates whether the corrosion layer is passivating. It is also possible to draw conclusions about the composition of the scale. In addition, the copper segments can be subjected to visual or microscopic inspection. **The results presented show that the corrosion rate is not constant, but depends on the properties of the water, the copper surface, the operating conditions, and, in particular, the age of the copper pipes.**

4. Determination of copper release in accordance with EN 15664-1

4.1 Experiment description

EN 15664-1 is a standard that describes the design and operation of systems for testing the corrosion of metals and alloys. Following the test, the release of metals from corroding metallic materials can be evaluated in accordance with the UBA's metal evaluation criteria (Annex 1) [4]. The test simulates consumption behavior in a drinking water installation for four people, represented by an operating regime in which periods of stagnation and water withdrawal alternate. The test involves the parallel examination of three test tubes. According to the standard, the test must be conducted at a room temperature of (20 ± 5) °C and with a water pressure of at least 3 bar. To reliably meet the

requirements, particularly those relating to sampling, a microprocessor-controlled test rig is necessary to control the valves for water flow in the test tubes and pipes, and to log the processes.

In accordance with EN 15664-1, metal concentrations in the contact water are determined after 4, 8, 12, 16, 21, and 26 weeks. To this end, the concentrations of eight samples are analyzed for the respective stagnation periods (two samples after 0.5 and 1 hour, and one sample each after 2, 4, 8, and 16 hours). Subsequently, the mean element concentrations (MEPa(T)) of the three pipes is calculated.

In addition to these complete sampling procedures, 4-hour stagnation samples are taken weekly from each test and control line throughout the test period and analyzed. The arithmetic mean values of the 4-hour stagnation samples are calculated for the analyzed elements from the three pipes.

MEP(T) values are important because they are based on multiple samples, and each value can be verified by graphically representing metal concentrations against stagnation times (see Chapter 4.4). On the other hand, the weekly development of metal concentrations in the 4-hour stagnation samples indicates whether the reference value for a given metal is met after a specific operating period. If the control line made of stainless steel (EN 10088-1, material no. 1.4401) contains dissolved metals, then those metals originate probably from the test water. In this case, the stagnation sample values must be adjusted. Furthermore, EN 15664-1 specifies maximum values for copper, iron, manganese, and zinc in test water.

The UBA's evaluation criteria for metals establish reference values for elements that differ from the parameter values set out in the EU Drinking Water Directive (DWD). For example, the reference value for copper is 1.8 mg/L, as opposed to the parameter value of 2.0 mg/L.

According to the UBA's metal assessment criteria [4], copper pipes are suitable for local water, based on a reference value of 1.8 mg/L copper and a weighting factor of A = 1, provided the two criteria A and B are met:

Criterion A is considered satisfied if:

(1) the mean value (MEPa(T)) is ≤ 1.8 mg/L for the sampling time points (T) at 16, 21, and 26 weeks.

Criterion B is satisfied if the element concentration does not increase again. One of the following requirements must be met:

(II) MEPa(T) decreases between pairs of sampling time points (12, 16), (16, 21), and (21, 26); or

(III) A regression line for 4-hour stagnation samples taken after the 12th week shows no upward trend; or

(IV) The mean value of 4-hour stagnation samples for weeks 16 to 26 is less than or equal to half the reference value (0.9 mg/L for copper).

If criterion B is not met, the test may be extended for up to one year.

4.2. Test setup

The tests were conducted using a rig test in accordance with EN 15664-1 from the DVGW Technology Center Water in Karlsruhe. For each water, the installation was set up with two parallel test pipes made of copper and one control pipe made of stainless steel. A corresponding corrosion test rig is shown in Figure 6.

The copper pipes, conforming to EN 1057 [5]—which had a length of 5 m, an inner diameter of 13 mm, an inner surface area of 0.204 m², and a volume of 0.663 L—were used in the test rig.

Figure 6. Corrosion test rig in accordance with EN 15664-1 from TZW, Karlsruhe.

4.3. Test procedure

After assembly and flushing, the test rig was checked thoroughly for leaks and functionality. Then, with two pipes for each water instead of three, as specified in EN 15664-1, the rig was put into operation and ran for 28 weeks, using 145 liters of test water per pipe per day. The same three water qualities used in the first trial were employed (see Table 1). During the test period, the average temperature of the test waters (15 ± 1 °C) met the standard's requirements.

In this test investigated the release of copper by analyzing the contact water in samples collected automatically. The metal concentrations in the contact water samples were determined after operating for 4, 8, 12, 16, 20, 24, and 28 weeks, which differs slightly from the standard. Additionally, a 4-hours stagnation sample was examined for each pipe every week for the same range of elements.

After each automated sampling sequence, the samples were stabilized with nitric acid. The subsequent elemental analysis was performed in accordance with EN ISO 17294- 2 [20] using an Agilent 7900 ICP-MS and MassHunter 4.2 software (Agilent Technologies Germany GmbH & Co., Waldbronn, Germany). In this series of tests, the stagnation samples were examined for concentrations of copper, phosphorus, silicon, and other elements relevant to water characterization. Since the samples from the stainless-steel reference pipes did not contain significant copper concentrations, no correction was necessary.

4.4. Results and interpretation

The corrosion test rig operated without any problems. The MEPn(T) concentration curves were constructed over time from the eight concentrations of the sampling sequence (see Figure 7). The arithmetic mean values of copper, MEPa(T), were calculated from the two MEPn(T) values of the two test pipes.

Stagnation time (h)	Cu in Water 2, Line 2.1 (mg/L)	Cu in Water 2, Line 2.2 (mg/L)	Cu in Water 3, Line 3.1 (mg/L)	Cu in Water3, Line 3.2 (mg/L)
0.5	0.61	0.59	1.02	1.02
0.5	0.57	0.56	0.96	0.96
1	0.98	0.93	1.6	1.61
1	1.11	1.07	1.8	1.78
2	1.57	1.53	2.63	2.64
4	2.46	2.38	3.66	3.86
8	3.17	3.1	4.24	4.35
16	3.16	3.57	4.1	3.7
***MEP*n(T)**	**1.70**	**1.72**	**2.50**	**2.49**
***MEP*a(T)**	**1.71**		**2.50**	

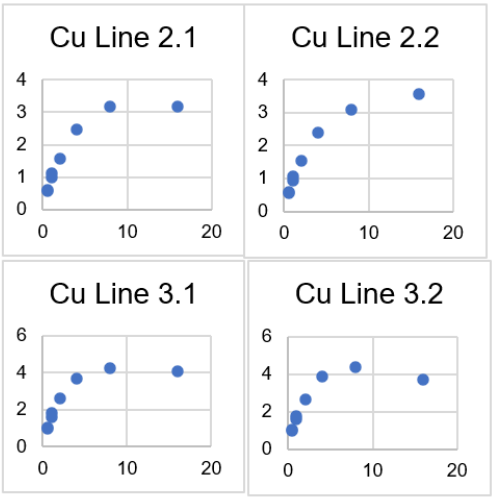


Figure 7. Example calculation of the *MEP*n(*T*)- and *MEP*a(*T*) values for Water 2 and 3 after 16 weeks of operation. The stagnation curves have an abscissa of hours and an ordinate of copper concentration in mg/L.

The development of *MEP*a(*T*) values over time is presented in Figure 8 for the three test waters. The increased copper release during the first few weeks is clearly visible. After 16 weeks, only Water 2 was below the reference value; Water 1 and Water 3 fell below it after 20 weeks. Water 3 had the lowest MEPa(T) value after 24 weeks. **According to criterion A I, only Water 2 was suitable for use with copper pipes.**

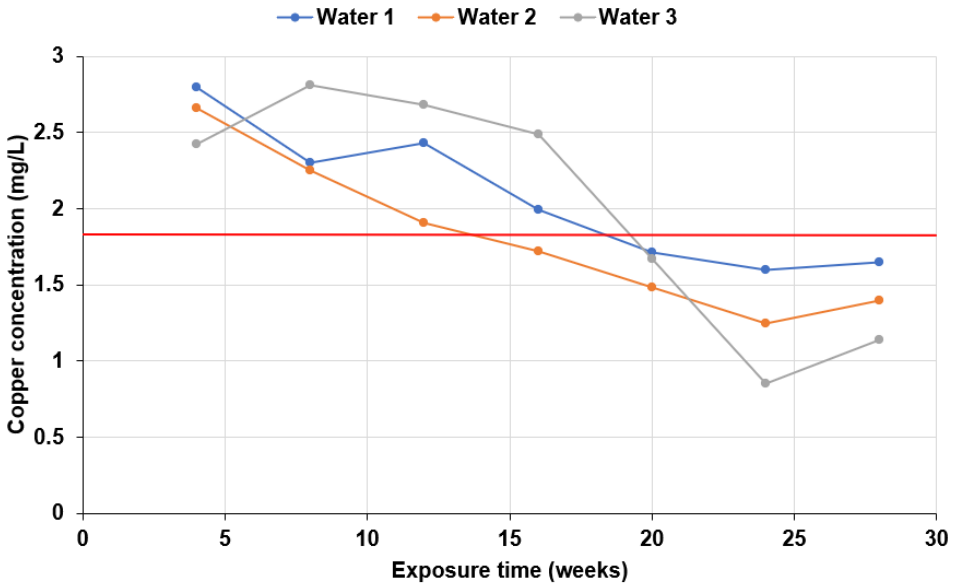


Figure 8. Graphical representation arithmetic mean values for copper according to EN 15664-1, red line: Reference value according to UBA [4].

For criterion B II, the MEPa(T) values for Water 2 were compared in pairs beginning in week 12. The trends for the pairs {12, 16}, {16, 20}, and {20, 24} were downward, while the trend for {24, 28} was upward. **Consequently, Water 2 did not meet criterion B II**.

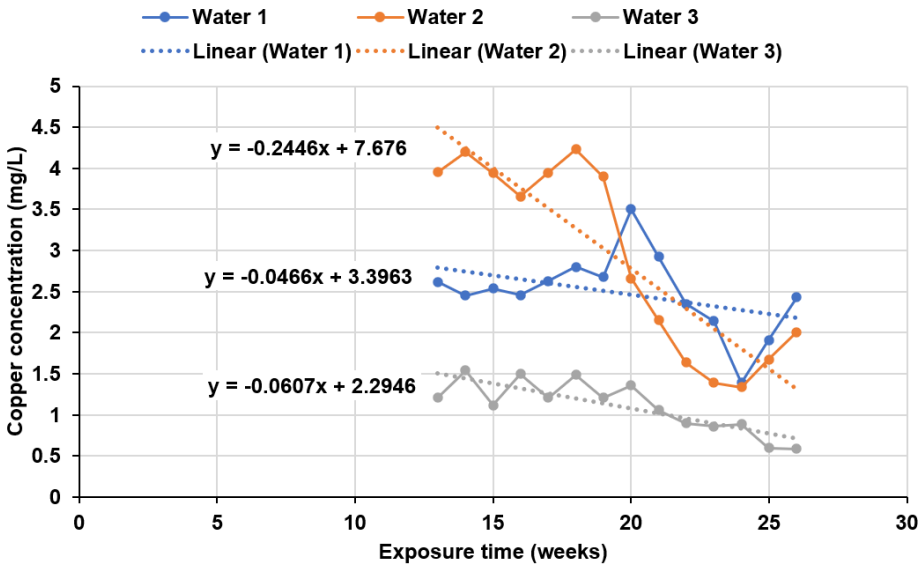


Figure 9. Graphical representation of 4-hour stagnation samples > 12 weeks according UBA evaluation, red line: Reference value according to UBA.

Criterion B III allows for the assessment of the trend in mean 4-hour stagnation samples, as shown in Figure 9. **The curve for Water 2 exhibited a negative slope from the 13th week onwards, thereby meeting Criterion B III.**

Alternatively, Criterion B IV can be applied to evaluate Water 2. The mean value of the 4-hour samples collected between the 16th and 26th weeks was 1.07 mg/L. This value exceeds half of the parameter value for copper (0.9 mg/L). **In this case, Water 2 failed to meet Criterion B IV.**

As the copper concentrations in Waters 2 and 3 rose sharply after the 24th week, the test period was extended. This revealed that the reference value for copper was not consistently met even after 52 weeks. Thus, copper was unsuitable as an installation material for the three test waters, even though the waters complied with the requirements of the metal assessment guideline regarding pH and TOC.

4.5. Summary

The standard test according to EN 15664-1, Annex 1, used to determine the compatibility of commercial copper materials or copper alloys with local drinking water, is very complex. Numerous samples of inlet and stagnant water must be regularly monitored. One advantage is that the test generally yields reliable and recognized results regarding metal release. Furthermore, the recommendations derived from these results protect the water supplier against recourse claims in the event of corrosion problems within the drinking water installation. Moreover, after the test is complete, the copper materials can be retrieved and prepared for examination using surface analysis techniques, such as microscopy. In this case, the results indicate that, even though the water quality requirements regarding pH and total organic carbon (TOC)—based on the UBA's metal evaluation criteria [4]—were met, copper was likely unsuitable for the installation with the three test waters. This confirms the high copper release rates observed in the first experiment.

5. Determination of copper release under stagnation in a closed-loop apparatus [12]

5.1 Experiment description

In addition to the copper release determination described in the previous chapter, this experiment involves removing and examining a test pipe that is permanently exposed to test water under stagnation conditions at specific times. This examination takes place

in a closed-loop apparatus with a very low flow rate to precisely monitor changes in the test water without significantly influencing the corrosion processes [21,22,23].

The time-dependent change in metal concentration in the test water is typically monitored through discontinuous sampling and analytical testing [24, 25]. A better alternative is continuous in-line measurement of copper(II), since this method does not alter the metal-to-stagnant water ratio, and corrosion-related oxygen consumption can be reliably determined by excluding contact with air. For copper determination, photometric evaluation of the absorption band of the neutral copper carbonate complex $[CuCO_3]^0$ at 280 nm is suitable [26]. Copper carbonate is not known as a solid substance, but in water containing hydrogen carbonate, it is the most important copper species in terms of concentration in the pH range from 6 to 8 (see Equation 9) [27].

$$Cu^{2+} + HCO_3^- \leftrightarrows [CuCO_3]^0 + H^+ \quad (9)$$

Since variations in ion concentrations (particularly bicarbonate) and pH can influence photometric analysis, the photometric determination of copper in test water requires calibration. To this end, absorbance values are determined as a function of copper(II) concentration. Additionally, it is recommended that the copper concentration be measured using a reference method (e.g., ICP-MS) after the stagnation period.

Determining the decrease in oxygen concentration within a closed apparatus allows for evaluation of the current corrosion ratee. Continuous measurements of pH, electrical conductivity, and temperature enable monitoring of the corrosion process.

5.2. Test setup

A closed-loop apparatus was assembled from the following components:

- a peristaltic pump with 0.76 mm inner-diameter Tygon tubing;
- a thermostat for the copper pipe under test;
- an UV/Vis spectrometer with flow-through cell; and
- a four-neck flask (100 mL) serving as a water reservoir equipped with sensors to measure oxygen (O_2), pH, electrical conductivity (E.C.), temperature, and a pierced, gas-tight stopper with inlet and outlet ports connected to the pump;
- an electronically controlled magnetic stirrer; and
- two silicone stoppers fitted with Teflon tubing for connecting the test tube.

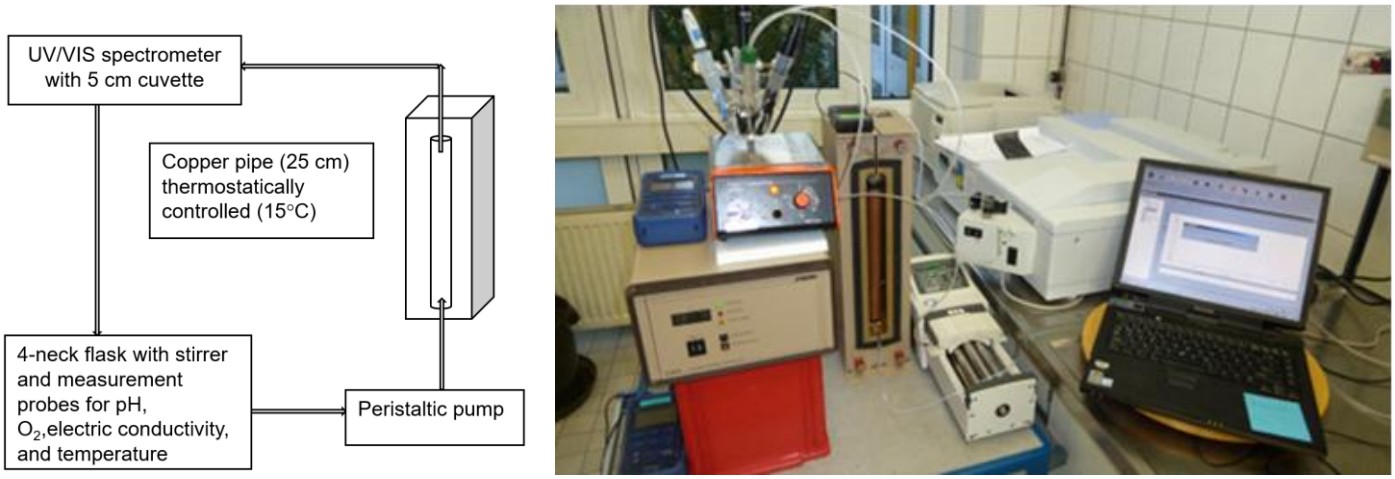


Figure 10. Closed-loop apparatus for measuring copper release during stagnation, **(a)** schematic setup, **(b)** laboratory set up.

A schematic diagram of the apparatus used is shown in Figure 10a, while the laboratory setup—with the thermostat housing open—is depicted in Figure 10b.

The closed system comprised a peristaltic pump (model 205U Watson Marlow, Rommerskirchen, Germany) with a flow rate of 0.54 l/h, an S4010 column thermostat with a thermocontroller from Sykam, Fürstenfeldbruck, and an UV/VIS spectrometer (Lambda 35 spectrophotometer with WIN-LAB software, version 6.0.3, PerkinElmer Life and Analytical Sciences, Shelton, CT, USA). Quantitative UV measurements were performed at 280 nm using a 50 mm flow cell (high-performance quartz glass 200–2500 nm, cat. no. 176700, volume 2.25 ml, Hellma GmbH & Co. KG, Müllheim, Germany). The electrodes for electrical conductivity (E.C.), pH, and an optode for oxygen (O_2) were installed in a gas-tight the four-neck flask. The in-situ parameters were measured and recorded using a Multi 3430 IDS, to which the FDO® 925 (O_2), TetraCon® 925 (E.C.) and SenTix® 980P (pH) sensors from WTW, Weinheim, Germany, were connected. O_2 was measured in accordance with ISO 17289 [16], E.C. in accordance with EN 27888 [17], pH in accordance with EN ISO 10523 [18], and temperature in accordance with DIN 38404-4 [19]. Samples for the analysis of total copper were taken from the flask immediately after the end of stagnation and acidified to 5% by mass with concentrated nitric acid. Elemental analysis was performed in accordance with EN ISO 17294-2 [20] using an Agilent 7900 ICP-MS and MassHunter 4.2 software (Agilent Technologies Germany GmbH & Co., Waldbronn, Germany).

Three seamless copper tubes from KME (Sanco R250)—each 25 cm long with an inner diameter of 26 mm, conforming to EN 1057 [5]—were used for the experiments. Based on these dimensions, the calculated internal surface area was 0.0196 m² and the volume was 0.123 L.

5.3 Calibration for the photometric determination of copper

A copper(II) stock solution (c = 1,000 mg/L) was prepared by dissolving 0.532 g of copper(II) chloride dihydrate (Merck, p.a. grade) in 250 mL of deionized water. Copper calibration solutions with concentrations ranging from 0.2 to 2.0 mg/L were prepared by adding aliquots of the stock solution to test water. The corresponding absorbencies were determined photometrically at 280 nm with a slit width of 1 nm. The obtained data were fitted linearly, and the method parameters listed in Table 3 were calculated.

Table 3. Photometric determination of copper via the $[CuCO_3]^0$ complex.

Method Parameter	Value
Calibration Range (mg/L)	0.2 - 2.0
Sensitivity (Slope) (L/mg)	0.1779
Residual Standard Deviation	0.0061
Detection Limit (mg/L)	0.077
Quantitation Limit (mg/L)	0.27
Method Coefficient of Variation (mg/L)	0.034
Correlation Coefficient	0.9986

5.4. Test procedure

The pipe sections were installed in the apparatus (Figure 1) and exposed to the waters described in Table 1 at a flow rate of 130 - 140 L/d each. After a three-week adaptation phase, the sections were removed for the first time, installed in the closed-loop apparatus, and tested for copper release. For the stagnation phases, 10-liter samples of each water were collected before the first measurement began. The samples were stored in a refrigerator at 5 °C to minimize changes in the water's properties during the stagnation experiments.

The flow in the flow-through apparatus was stopped and the specific pipe to be examined was removed. It was then emptied, installed in the thermostat of the recirculating apparatus, and brought to a temperature of (15.0 ± 0.1) °C. The flask was then filled with test water, and the photometer was zeroed using this water. Then, the pipe section was filled with test water using the peristaltic pump. Then, a magnetic stir bar was placed in the flask. The flask was filled with test water and sealed airtight with the measuring probes and the inlet/outlet stopper. The stirrer motor beneath the flask was set to 200 rpm, and the UV and in-situ measurements were initiated. The UV/VIS spectrometer parameters in kinetic mode were as follows: wavelength, 280 nm; slit width, 1 nm; measurement interval, 60 s; and measurement duration, 8 h.

After the measurement, the stagnant water was sampled, and the copper concentration was analyzed via ICP/MS. Finally, the copper pipe section was reinstalled in the flow-through apparatus. The photometer data (time-dependent absorbance values) and sensor parameters were combined and evaluated.

5.5. Results and interpretation

5.5.1. Water 1 (oxidatively treated)

Figure 11 shows the temporal progression of the photometrically determined copper concentration and the in-situ parameters for Water 1 during the 2nd stagnation phase (4th week). At the beginning, the copper concentration rose almost linearly. The slope then decreased, and the copper value reached a maximum of 1.92 mg/L after about five hours (18,000 s) before slowly falling again. After eight hours (28,800 s), a value of 1.85 mg/L copper was reached. The concentrations listed in Table 4 were obtained after four and eight hours of stagnation.

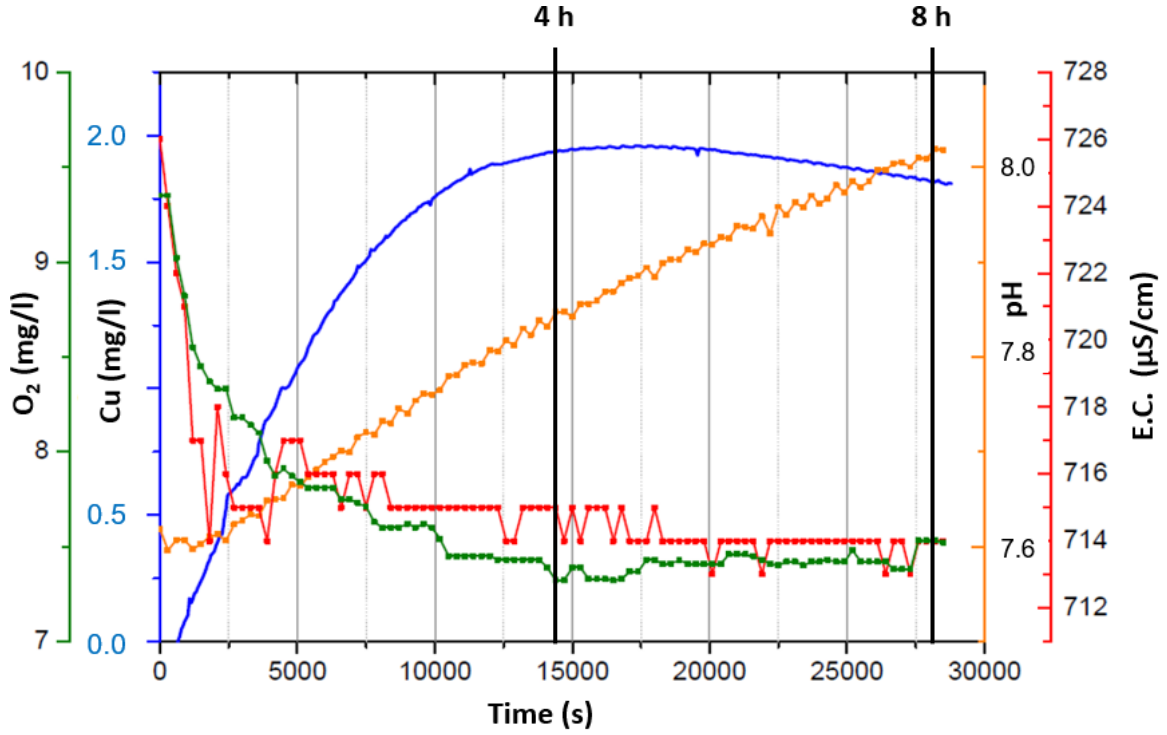


Figure 11. Stagnation phase of the copper pipe after 4 weeks of continuous exposure in Water 1.

This concentration curve for copper is known as the maximum curve from the literature [13, 21] and can be explained as follows: Initially, the release of copper into the water dominated. After 5 hours, the incorporation of copper ions into the surface layer exceeded the solubility of the copper corrosion products, causing the copper

concentration in the solution to decrease. The oxygen concentration dropped after 5 hours and then remained almost constant at a high level of 7.5 mg/L for up to 8 hours. The E.C. of the water was 726 µS/cm which fell to 714 µS/cm. This can be explained by initially complexation to form a neutral, dissolved copper carbonate complex and subsequently by the incorporation of ions into the surface layer. Corrosion reduces oxygen and forms hydroxide ions, causing the pH value to rise according to Equation 10. The approximately linear increase of pH from 7.6 to 8.1 can be explained by the definition of pH as a logarithmic value.

$$O_2 + 4\ e^- + 2\ H_2O \rightarrow 4\ OH^- \qquad (10)$$

5.5.2. Water 2 (naturally treated)

For Water 2, the maximum copper concentration was reached after 20,500 s (6.56 h) at 2.2 mg/L. The concentration then fell slightly again (see Figure 12). The continuous decrease in E.C. from 717 µS/cm to 704 µS/cm can be explained by the sorption of ionic water constituents into the surface layer.

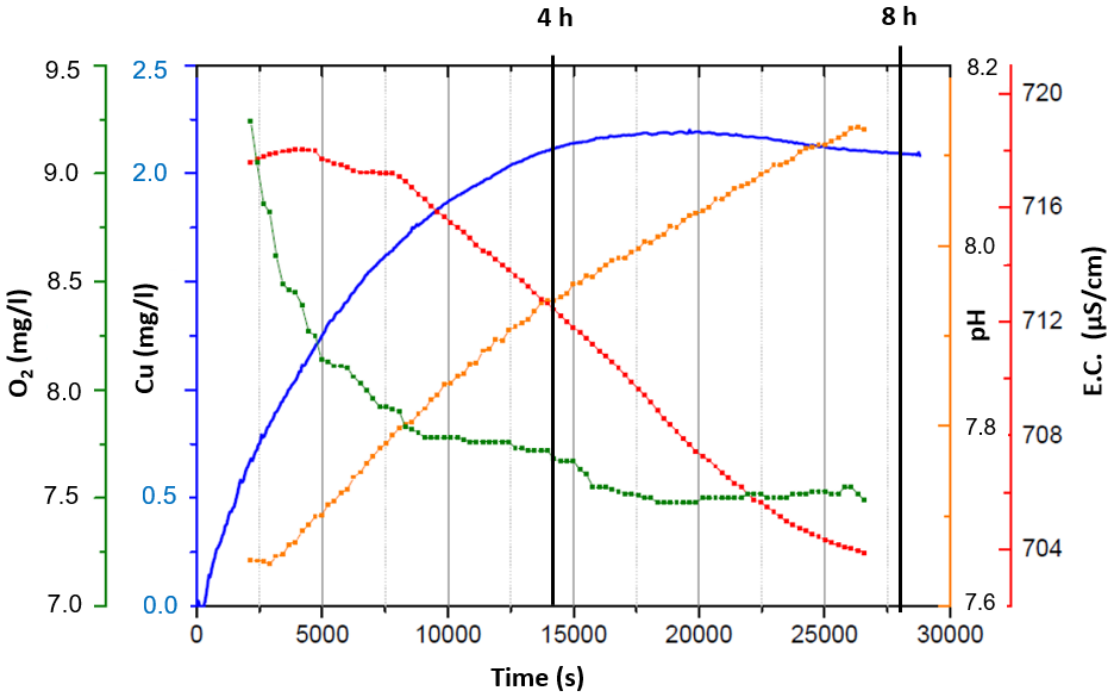


Figure 12. Stagnation phase of the copper pipe after 4 weeks of continuous exposure in Water 2.

5.5.3. Water 3 (partially demineralized)

During the eight-hour stagnation phase, the softened Water 3 did not reach a plateau in copper concentration (see Figure 13). However, after just three weeks of installation, copper concentrations were lower than in Water 1 and Water 2 (see Table 4). The increase in pH from 7.7 to 8.3 is the highest of the three measured values presented, as the water—being lower in ions—is less buffered. The initial rise in E.C. is caused by the scaling of the corresponding axis.

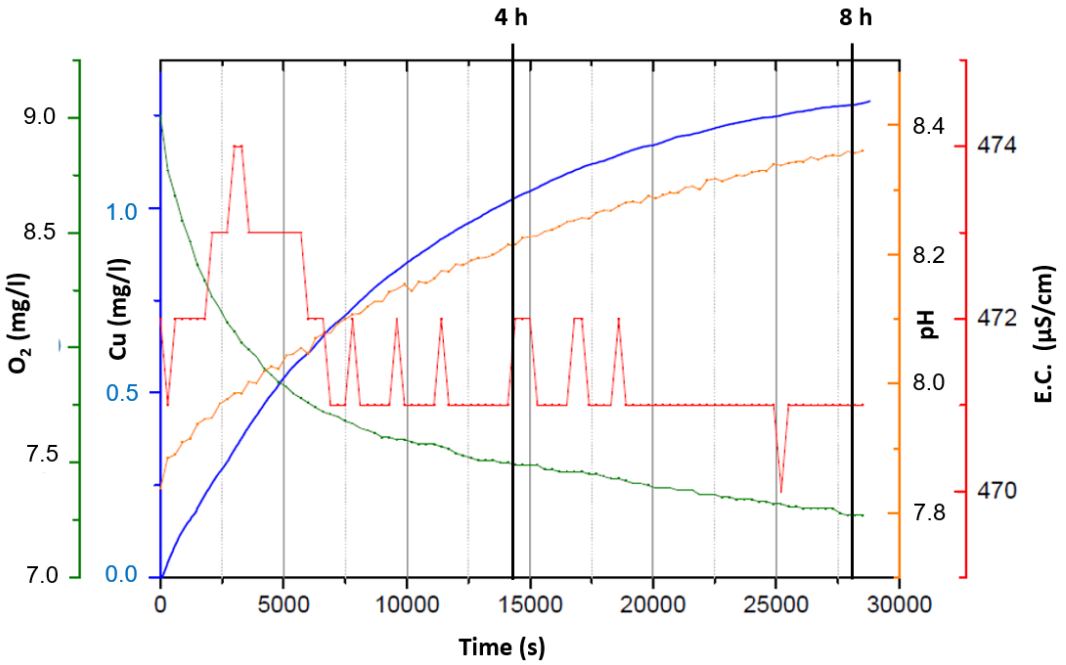


Figure 13. Stagnation phase of the copper pipe after 3 weeks of continuous exposure in Water 3.

The measured copper concentrations after 4-hour and 8-hour for all stagnation phases are presented in Table 4.

Table 4. Copper concentrations in stagnant water after 4 and 8 hours.

Week	Stagnation time (h)	Copper in Water 1 (mg/L)	Copper in Water 2 (mg/L)	Copper in Water 3 (mg/L)
3	4	1.93	1.95	0.91
3	8	1.81	2.02	1.29
4	4	1.92	2.12	-
4	8	1.85	2.08	-
5	4	1.80	1.95	1.12
5	8	1.84	2.02	1.31

A comparison shows that, even if the equilibrium value was not reached after eight hours of stagnation, softened Water 3 was significantly less corrosive to copper than Water 1 and 2. This was due to the lower ion concentration in Water 3. In contrast, Water 1 and Water 2 did not differ significantly from each other in terms of stagnation behavior. Therefore, it can be concluded that oxidative treatment had little influence on the corrosion behavior of copper pipes.

5.6. Comparison of EN method and simplified method for copper release

To compare the results of the EN 15664-1 method with those of the closed-loop apparatus, one must take into account the different area-to-volume ratios. The ratio for the EN test rig was 307.7 m^{-1}, while the ratio for the closed-loop apparatus was 153.8 m^{-1}. Dividing these values yields a correction factor of 2, which must be applied to the closed-loop test results for comparison purposes (see Table 5).

Table 5. Comparison of copper concentrations from the EN method and the closed-loop apparatus.

	Copper concentrations after 4 weeks (mg/L)					
Stagnation time (h)	Water 1, EN	Water 1, closed-loop standardized to EN	Difference in methods (%)	Water 2, EN	Water 2, Closed-loop, standardized to EN	Difference in methods (%)
4	3.66	3.84	4.89	3.93	4.24	7.9
8	4.04	3.69	-9	3.72	4.16	11.9

[1] The measurement of Water 3 after 4 weeks could not be evaluated.

After correction, the measured values from the closed-loop method align with the EN 15664-1 values within an uncertainty of ±10%. However, the EN method values are considered more reliable. Following correction, the measured values from the closed-loop system align with the values specified in EN 15664-1 within an uncertainty of ±10%. However, the values obtained via the EN method are considered more reliable. One possible reason for the discrepancy is that the test pipe was removed from the apparatus shown in Figure 1 and briefly ran dry during the process, which may have altered the pipe's surface. To prevent this in the future, a valve should be installed below the test pipe; this would allow the current test water to be retained, thereby avoiding the need to change the water.

Furthermore, the 4-hour stagnation values obtained using the closed-loop apparatus should be comparable to the "S1 sample" defined in the sampling guidelines of the German Environment Agency [28]. This would enable a comparison with DWD parameter values, such as 2 mg/L for copper.

5.7. Summary

Stagnation tests on permanently exposed copper pipes produced two typical stagnation curves. For Water 1 and Water 2, curves with maxima that subsequently dropped versus equilibrium values were observed. There was no significant difference in stagnation behavior between the two waters. Therefore, it can be inferred that the type of treatment, whether oxidatively or naturally treated, had little influence on the corrosion behavior of the copper pipes in this instance. In contrast, Water 3 exhibited a continuously rising curve with a decreasing slope and showed no peak within the measurement period. However, after four and eight hours, partially demineralized Water 3 showed lower copper concentrations than Water 1 and Water 2, which displayed similarly high copper levels. To compare the results obtained using the closed-loop apparatus with those specified in the EN 15664-1 standard, one must consider the surface-area-to-volume ratio. A deviation of ±10% from the EN method was observed for the closed-loop method, though reducing this variance appears possible.

In summary, the simplified method for assessing copper release provides valuable information about the corrosion process and potential limit value exceedances while requiring significantly less effort.

6. Conclusion of the investigations

The corrosion of copper and copper alloys affects the longevity of components made from these materials, as well as the quality of drinking water that comes into contact with them. To evaluate this issue, the method described in Chapter 3 for determining the corrosion rate based on material loss from samples can be applied. This method shows when and if the tested material transitions into a state of uniform corrosion. Only minimal financial and personnel resources are required.

Regarding copper release, which is relevant for drinking water quality, a simplified test can be performed in a closed-loop apparatus, as described in Chapter 5. This test can be easily implemented in an existing chemical laboratory.

If these tests reveal abnormalities or parameter value exceedances, more extensive and costly tests should be carried out for reference purposes using a test rig in accordance with EN 15664-1 (see Chapter 4).

Funding

This study was externally funded by a water supplier.

Acknowledgements

The authors thank everyone who contributed to this work and the reviewer for the valuable suggestions.

AI Support

Google Translate and DeepL Write were used for word processing of this article.

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