Copper corrosion: understanding and modelling general corrosion

T.H. Merkel
Weberstube 3, 55232 Alzey, Germany (E-mail: till.merkel@t-online.de) formerly at DVGW-Water Technology Center, Karlsruher Straße 84, 76139 Karlsruhe, Germany (E-mail: info@tzw.de)

Abstract Based on a literature study and on pipe-rig studies a mechanism is proposed which subdivides general corrosion of copper into three subprocesses: oxidation, scale formation and dissolution. The subprocesses are further characterized and a mathematical model is built on the identified kinetic rate laws. Finally, conclusions for optimising corrosion control strategies are discussed.

Keywords Copper; drinking water; general corrosion; mechanism; modellingization

Introduction
With the promulgation of the new EC drinking water guidelines and the German drinking water directive (TrinkwV, 2001) the parameters were grouped into two sections: parameters which do not change during water distribution and parameters which do change. Metallic materials commonly applied in domestic installations such as copper, nickel or lead belong to the second group. Moreover, the parametric values for these elements have to be met at the consumer’s tap. For these reasons, the attention of water utilities, health authorities and manufacturers is drawn towards the processes in this part of the distribution system.

In Germany a new user guideline was defined in the national standard DIN 50930-6 which supplements the restrictions of the drinking water directive for copper, brass, galvanized steel, etc. and thus defines the state-of-the-art in the application of metal materials in contact with drinking water. However, in some cases a clear decision on the applicability of a material is not possible (e.g. lack of scientific understanding of the processes, borderline situations, changing water qualities) so that this decision has to be based on the test procedure DIN 50931-1. This standard provides the set-up of a pipe-rig, a flow protocol as well as a sampling and evaluation procedure in order to monitor the metal concentrations in drinking water over a two year period. The interaction of the metal material with the drinking water is evaluated after stagnation periods where higher concentrations were determined than in the flowing water.

A literature study on the topic “copper concentration during stagnation” yielded no clear results. Three different shapes of the copper concentration-time curve (stagnation curve) were identified (Figure 1), but none of the existing mechanisms on general corrosion of copper could explain the experimental findings.

On this background, the literature study was extended from drinking water corrosion to atmospheric corrosion, electrochemistry and general inorganic chemistry where over 500 articles and books were analysed in order to collect ideas on the corrosion mechanism and to identify analytical, experimental and methodical needs for the laboratory study. A special focus was set on mechanistic studies and articles on the composition and role of corrosion scales on the surfaces.

A detailed analysis revealed the necessity to differentiate between short-term and long-term effects. A reliable interpretation of experimental results may only be successful when
fast chemical and physical effects such as oxidation or mass transfer and slow changes in composition and structure of corrosion scales are considered at the same time. Corrosion takes place at the solid/liquid interface which is changed by and which influences the corrosion processes. For this reason, short- and long-term effects had to be studied in the experimental setups and the changes of the properties of the corroded surfaces had to be monitored and included in the interpretation of the data from the stagnation experiments.

Experimental and analytical methods

The experiments were designed around the pipe-rig concept for studies on general corrosion according to DIN 50931-1. New copper pipes (hard-drawn pipes, internal diameter 13 mm) were exposed to the test water (see Table 1) where water was flowing for 1 or 2 minutes at a flow rate of 300 L/h. 22 flow periods took turns with stagnation periods from 15 min to 8 hours, thus 145 L/day were sent through each pipe. This operation protocol provided the basis for reproducible results.

Two 5 m pipes were installed in series which were sampled separately for dissolved copper and dissolved oxygen after stagnation; the set-up was completed by a 2 m pipe from which weekly samples for surface analysis were taken. The pipe-rig and the operation protocol represented the consumption pattern of a kitchen tap in a four people household and were applied to study the total process “copper corrosion in drinking water installations” by providing close-to-real-life stagnation curves and pipe samples. Seven experimental series were made at room temperature (water entered the pipes at 12°C and was heated up to 22°C by the laboratory air during stagnation) and at constant temperature (5, 12, 18 and 25°C). The sampling protocol of the standard DIN 50931-1 was supplemented with long-term stagnation periods up to 5 days in order to identify and study possible steady-state concentrations.

The first results lead to the hypothesis that copper concentration was not controlled by a single process such as solubility or mass transfer as often stated in the literature but by several parallel subprocesses. In order to further characterize these subprocesses a closed-loop pipe-rig (parameters: flow rate and temperature) and batch reactors with powdered material and coated copper coupons (parameters: temperature and water composition)
were designed. Solid corrosion by-products for the batch experiments which can be found as scale constituents were synthesized as powder or as coatings on copper coupons.

In addition to the determination of stagnation curves for oxygen and copper the development and characteristics of corrosion scales during operation was monitored. For this purpose, the extended-focus technology was developed (in cooperation with Leica-Microsystems, Wetzlar/Germany) which enabled us to create in-focus high-resolution images and to determine the surface relief. Based on this technology the surface coverage with malachite was determined by image analysis, and detailed examination at an ESEM (environmental scanning electron microscope) was prepared. A wet-chemical pickling method to selectively dissolve bi- and mono-valent copper compounds from the pipe surface, metallographic preparation methods for the determination of scale structure and thickness and a micro-XRD system for identifying the crystalline scale constituents completed the analytical means.

Results of long-term stagnation experiments in pipe-rigs according to DIN 50931-1

In addition to the three curve shapes from the literature (Figure 1) the long-term stagnation experiments yielded two other types of stagnation curves (Figures 2 and 4). Figure 2 (left) represents the so-called “characteristic” curve which was found in 34 of 36 cases: after a fast increase the copper concentration reached an intermediary maximum, followed by a slower decline down to a stable concentration which was found to be similar to the solubility of the basic cupric carbonate malachite in the test water. The maximum decreased with operation time and appeared earlier.

The oxygen concentration decreases exponentially with stagnation time (Figure 2, right as relative concentration) which can be described by a first-order kinetic rate law. In contrast to the stagnation curve for dissolved copper the kinetics of the oxygen reaction did not change with operation time.

Further data interpretation yielded the explanation that the characteristic curve is the result of competing sink and source reactions for dissolved copper. So the total process was subdivided into three subprocesses: the oxidation of metallic copper and cuprous compounds, the dissolution of existing scales and the formation of solid corrosion by-products from the oversaturated water.

Copper oxidation was identified to be the major source for dissolved copper. However, the oxidized metal is not transferred completely into the aqueous phase, only the fraction $\alpha$ can be found as dissolved copper. The molar yield of the cupric ion formation from the oxidation of copper metal with oxygen may reach a maximum value of 2, so that the range of the yield is $0 \leq \alpha \leq 2$. The remaining fraction ($2-\alpha$) is integrated into the corrosion scale immediately after its formation at the solid-liquid boundary by solid phase reaction or

![Figure 2](https://iwaponline.com/wst/article-pdf/49/2/63/420424/63.pdf)

**Figure 2** Characteristic stagnation curve for dissolved copper (left) and normalized oxygen concentration (right). First series at room temperature after 9 (○), 10 (+), 11 (▲), 13 (■) and 14 (□) weeks of operation.
precipitation from the pore water (primary scale formation). Crystallization from the oversaturated bulk water is another important though slower pathway for reducing the copper concentration and shall be called secondary scale formation.

XR-microdiffraction on pipe samples from different waters only identified two crystalline phases: the reddish-brown cuprous oxide (\(\text{Cu}_2\text{O}\) – cuprite) and the blue-green basic copper carbonate (malachite – \(\text{CuCO}_3\cdot\text{Cu(OH)}_2\)). Cuprite already forms in the atmosphere within several hours of exposure and is also the first product to be formed on the copper surface in water pipes. The homogenous film reaches a thickness of less than 1 \(\mu\)m, in rare cases well-shaped crystals can be found. The cuprite mass on the surfaces does not significantly change with operation time. Malachite forms globular structures (diameter 40 to 100 \(\mu\)m) which usually do not grow in size but in number. Figure 3 shows the typical appearance of a corroded surface in the pipe-rigs (see also (Merkel, 2001)). The high-resolution light-microscopical image on the left hand-side shows the malachite structures on the surface, the images on the right hand-side give an overview and serve as the basis for quantifying the surface coverage with malachite as a function of operation time.

The surface coverage malachite was found to increase with operation time while the copper concentration in the stagnation samples decreased. Though part of the surface was covered from the dissolved oxygen by the malachite layer a decrease in the kinetics of the oxygen reaction was not observed. Thus, the yield of the major source reaction remained unchanged. While the malachite coverage increased from 0 to about 80 per cent of the visible surface the oxygen consumption stayed at about 0.5 mg/(L h) over the whole operation time. According to this result the copper concentration during stagnation declined by crystallization of malachite from the oversaturated solution which is accelerated by the increase of nucleation points on the malachite covered part of the surface (Merkel et al., 2002).

The kinetics of the oxygen reaction seemed to be independent of the operation temperature while the kinetics of secondary scale formation increased with temperature.

In the case of the characteristic curve (Figure 2, left) total dissolved copper is only made up of dissolved cupric ions or complexes. At a temperature of 25°C a significant quantity of cuprous ion was identified within the first weeks of operation. In this particular and rare case the shape of the stagnation curve changed (Figure 4). After an initial inclination to an intermediary maximum the total copper concentration decreased below the limit of detection of the photometric method. When oxygen depletion was completed, total copper rose to a stable final concentration which is controlled by the solubility of malachite in the test water. In order to explain this curve, further processes need to be considered (see chapter “Corrosion mechanism and modelling”).

![Figure 3](https://iwaponline.com/wst/article-pdf/49/2/63/420424/63.pdf) Blue-green malachite structures on corroded copper pipe surfaces. (Left) light-microscope image, original size 189 × 142 \(\mu\)m, (right) malachite surface coverage after different operation times, original size 43.2 × 3.7 mm²
Results from the experimental studies of the subprocesses

Oxidation, scale dissolution and scale formation were identified as subprocesses of general copper corrosion. In the closed-loop experiments the kinetics of oxygen consumption were also found to follow a first-order kinetic rate law. Since there was no significant effect of hydraulics on the time constants of the rate law, the computed time constants for the oxygen reaction from closed-loop experiments and from stagnation experiments can be compared directly. The rates of the oxygen reduction and the metal oxidation are controlled by the chemical reactions.

In short-term experiments in the closed-loop system time constants for metal oxidation accelerated by a factor of 1.5 when temperature increased by 10°C. When using this figure for general conclusions it has to be considered that the examination in the closed-loop system is a short-term effect where parameter changes only affect the chemical reactions and mass transfer but do not influence the properties of the oxide film. In long-term experiments changes in temperature have an effect on both the chemical reaction and the oxide film. While the reactions were accelerated the properties of the oxide film retarded the oxidation, so that the overall effect of a temperature increase in the pipe-rig study was not significant.

According to the results of closed-loop experiments on malachite dissolution in oxygen-free water this subprocess is controlled by mass-transfer and can be described by a first-order kinetic rate law where the kinetic parameter can be derived from the technical correlations for mass transfer processes for pipe flow. Changes in temperature affect the viscosity of the water which was found to be the predominant effect on mass transfer rates. In supplementing batch experiments no effect of neutral salts, dissolved organic carbon and corrosion inhibitors (ortho-phosphate, poly-phosphate) on the mass transfer kinetics was observed.

In a second set of batch experiments the interaction of copper coupons which were coated with different corrosion by-products (oxides, hydroxide or basic salts) with oversaturated waters was examined. Crystallization of malachite was found to be the predominant mechanism of secondary scale formation which according to additional batch and stagnation experiments can be described by a first-order kinetic rate law with respect to the concentration of dissolved cupric species.

The batch experiments on the influence of water constituents on the kinetics of malachite formation revealed that the kinetic parameters of scale formation and scale dissolution have the same order of magnitude. The neutral salts NaCl and Na₂SO₄ do not affect malachite formation, significant retardation was found for ortho-phosphate (0 < c (phosphate-P) < 1 mg/L) and poly-phosphate (c = 0.01 mg/L phosphate-P). For both inhibitors a further increase in phosphate-P did not aggravate the effect. For a surface-waterborne dissolved organic carbon (bog-water from Hohlohsee, Schwarzwald/Germany) malachite formation increased as a function of concentration.
Finally, studies on the influence of temperature and water composition on the solubility of malachite completed the experiments. The derived equilibrium concentrations \([\text{Cu}^{II}]_{eq}\) were the basis for the data evaluation and the modelization work of the stagnation curves.

**Mechanism and mathematical model of general corrosion**

Based on the experimental findings on the kinetics of the subprocesses and the literature study a model of the corrosion mechanism was developed which describes the oxidation of metallic copper to mono- or bivalent copper as first step, secondly takes into account primary and secondary scale formation by precipitation of mono- or bivalent copper compounds, and thirdly includes scale formation. An estimation of the influence of radial diffusion yielded that the process is not controlled by mass transfer. In the general approach, sink and source reactions for three species (\(O_2\), \(\text{Cu}^I\) and \(\text{Cu}^{II}\)) have to be considered, which leads to a system of three coupled linear differential equations:

\[
\frac{d[O_2]}{dt} = -k_1'[O_2] - k_2'[\text{Cu}^I][O_2] - k_3'[O_2] \tag{1}
\]

\[
\frac{d[\text{Cu}^I]}{dt} = \alpha_1 k_1'[O_2] - k_{S,1} \cdot (\text{[Cu}^I]\) - [\text{Cu}^I]_{eq}) - k_2'[O_2][\text{Cu}^I] \tag{2}
\]

\[
\frac{d[\text{Cu}^{II}]}{dt} = \alpha_2 k_2'[O_2][\text{Cu}^I] + \alpha_3 k_3'[O_2] - k_{S,2} \cdot (\text{[Cu}^{II}] - [\text{Cu}^{II}]_{eq}) - k_{\text{syn}}[\text{Cu}^{II}] \tag{3}
\]

This system of linear differential equations may only be solved numerically and must be applied to describe the copper concentration curve in Figure 4 from the stagnation experiments at 25°C. Due to the high number of parameters the results of the numerical evaluation and the computed values have to be interpreted with caution. However, the calculated figures do make sense, which may serve as a proof that the corrosion mechanism and its mathematical formulation can be applied to describe the experimental results.

The characteristic shape of the stagnation curve (Figure 2, left) which was found for \(T \leq 18^\circ C\) can be represented with a simplified modelization approach. Since the concentration of monovalent copper can usually be neglected, Eq. (2) and all terms of the differential Eqs (1) and (3) which describe reactions and formation of cuprous species are removed from the system. Thus, the oxygen depletion can be represented by a simple first-order equation (Eq. (4)), and the copper concentration can be expressed in a closed form (Eq. (5)).

\[
[O_2](t) = [O_2]_0 \cdot \exp[-k_{ox} t] \tag{4}
\]

\[
[\text{Cu}^{II}](t) = [\text{Cu}^{II}]_{eq} \cdot (1 - \exp[-k_S t]) + [\text{Cu}^{II}]_0 \cdot \exp[-k_{St}] + \frac{k_{ox}}{k_{ox} - k_S} \cdot (\exp[-k_{St}] - \exp[-k_{ox} t]) \tag{5}
\]

Eq. (4) and (5) were applied to evaluate the data from the long-term stagnation experiments which yielded the characteristic curves from the pipe studies according to DIN 50931-1. When suitably combining the parameters \(k_{ox}\), \(k_S\) and \(\alpha\) the stagnation curves from the literature (Figure 1) can be modelled as well.

Based on these model equations the effect of two different ways of scale ageing on copper stagnation curves was simulated. With respect to the development of oxygen and scale kinetics with operation time, height and appearance of the concentration maximum
changed. These findings and their experimental verification in this study lead to conclusions on the scale properties from successive stagnation curves without examining the pipes with surface-analytical means.

**Summary**

The proposed corrosion mechanism and its mathematical formulation were successfully applied to describe copper concentration during stagnation and are based on the following key finding:

The concentration of dissolved copper during stagnation is determined by the action of three subprocesses: oxidation, scale formation and scale dissolution.

**Conclusions for corrosion control in water distribution systems**

Since oxidation, scale formation and scale dissolution are taking place simultaneously during general copper corrosion but at different reaction rates, all of them need to be considered when developing corrosion control strategies. Thus, choosing and applying a corrosion inhibitor is an optimisation process which may be facilitated by means and methods applied and developed in this study.

Additional experiments showed that copper release during flow periods (5 L/min, internal pipe diameter 13 mm) is dominated by malachite dissolution whereas copper release from oxidation can be neglected. In the case of a very slow water flow (dripping water tap) metal oxidation becomes the major source for dissolved copper.

Secondary scale formation, i.e. the precipitation from the oversaturated bulk water is mainly taking place during stagnation. After very long stagnation periods significant changes of scale properties and copper release may be observed because high amounts of malachite have been formed. A general conclusion from this research is that the dynamic system copper/corrosion scale/drinking water may be easily affected. For this reason, steady-state characteristics of the scale may only be found when changes in the operation mode, temperature and water composition are negligible. This statement also leads to the conclusion that copper installations where exposure to hard groundwater and soft surface water take turns do not develop stable scales and therefore may be highly vulnerable to a corrosion attack. The stability of existing corrosion scales with respect to water quality may be evaluated with the batch experiments in this study.

In order to decide on the probability of a corrosion attack the concentrations of both copper and oxygen should be determined in the stagnation experiments. If it is not possible to take samples for a complete stagnation curve, sampling after four hours stagnation and after fully flushing the system will give hints on the state of the system but do not fully replace the systematic study according to DIN 50931-1 and additional surface-analytical evaluation of the pipes. But even without surface analytical means the corrosion mechanism and the mathematical model provide some information on the surface characteristics when several successive stagnation curves are available and are interpreted with respect to the changes in the concentration maximum with operation time.

Finally, it is essential to hint at important restrictions of this corrosion mechanism. A major prerequisite is that a solid and stable compound of bivalent copper is formed which includes both the thermodynamics and the kinetics of crystallization. For this reason, general conclusions for all waters are not possible based on the presented data. For instance, the role of metastable solids such as cupric hydroxide deserves further investigation, the aging of existing solids with associated reductions in solubility also plays a role on some occasions. Further investigation which includes both the analysis of water quality data and surface analytics is necessary to get to a more general understanding of the process.
**Future perspectives**

The presented research work provides some insight into the dynamic system copper/corrosion scale/drinking water. Additional studies on the influence of water constituents on the kinetics of the oxygen reaction should complete the existing results. For this purpose it is necessary to further improve the coating procedures to create surfaces with reproducible features, which is the prerequisite for a systematic parameter study.

Furthermore, the role of dissolved and solid cuprous species remains unclear. In this study, total copper was determined photometrically. Although this method differentiates between mono- and bivalent copper it only offers qualitative hints on dissolved cuprous species. At this point, online polarography may serve as a suitable approach.

A very important drawback of all existing mechanisms and mathematical models is the fact that they do not enable us to get to make a long-term prediction on the changes of corrosion scales with operation time. According to the literature the cuprite film controls the metal oxidation, but the chemical and physical reasons for the development of n- or p-semiconductive properties or special morphologies (films or micro-crystals) are still unknown.

The introduction of the TOC as a design parameter for the applicability of copper in the German standard DIN 50930-6 opens up another set of questions on the influence of the organic carbon on the subprocesses and subsequently on copper release. The results from this research work may be considered in the interpretation of real-life data with caution, and they may serve as a starting point for a more detailed study of the issue.

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Symbols and variables

- $[\text{Cu}^I]$ concentration of dissolved cuprous species (mol/L)
- $[\text{Cu}^I]_{eq}$ concentration of dissolved cuprous species in equilibrium with monovalent copper compounds in the test water – mostly cuprite (mol/L)
- $[\text{Cu}^{II}]$ concentration of dissolved cupric species (mol/L)
- $[\text{Cu}^{II}]_{eq}$ concentration of dissolved cupric species in equilibrium with a solid cupric compound in the test water – mostly malachite (mol/L)
- $[\text{Cu}^{II}]_0$ concentration of dissolved cupric species in the influent (mol/L)
- $[\text{O}_2]$ concentration of dissolved oxygen (mol/L)
- $[\text{O}_2]_0$ concentration of dissolved oxygen in the influent (mol/L)
- $\alpha$ molar yield of metal oxidation with respect to the formation of dissolved $[\text{Cu}^{II}]$ with $0 \leq \alpha \leq 2$
- $\alpha_1$ molar yield of the reaction $\text{Cu}^0 \rightarrow \text{Cu}^I$ with respect to the formation of dissolved Cu$^I$ with $0 \leq \alpha_1 \leq 4$
- $\alpha_2$ molar yield of the reaction $\text{Cu}^I \rightarrow \text{Cu}^{II}$ with respect to the formation of dissolved Cu$^{II}$ with $0 \leq \alpha_2 \leq 4$
- $\alpha_3$ molar yield of the reaction $\text{Cu}_2\text{O} \rightarrow \text{Cu}^{II}$ with respect to the formation of dissolved Cu$^{II}$ with $0 \leq \alpha_3 \leq 4$
- $k'_1$ time constant of the reaction of dissolved $\text{Cu}^0 \rightarrow \text{Cu}^I$ (s$^{-1}$), where $k'_1 = k_1[\text{Cu}^0]$ and $[\text{Cu}^0] = 1$ mol/L
- $k_2$ time constant of the reaction of dissolved Cu$^I \rightarrow$ Cu$^{II}$ (L mol$^{-1}$ s$^{-1}$)
- $k'_3$ time constant of the reaction $\text{Cu}_2\text{O} \rightarrow \text{Cu}^{II}$ (s$^{-1}$), where $k'_3 = k_3[\text{Cu}_2\text{O}]$ and $[\text{Cu}_2\text{O}] = 1$ mol/L
- $k_{ox}$ time constant of the oxygen consumption (s$^{-1}$)
- $k_{S,1}$ time constant of cuprite formation (s$^{-1}$)
- $k_{S,2}$ time constant of malachite formation (s$^{-1}$)
- $k'_{syn}$ time constant of the synproportionization $\text{Cu}^{II} + \text{Cu}^0 \rightarrow \text{Cu}_2\text{O}$ (s$^{-1}$)
- $k_S$ time constant of the scale processes (formation or dissolution) (s$^{-1}$)