Copper corrosion in drinking water systems – effect of pH and phosphate-dosage

J. Dartmann*, B. Sadlowsky, T. Dorsch and K. Johannsen

Copper corrosion in residential plumbing installations can lead to an increase in copper concentration in drinking water as well as to leakages. Central water treatment steps such as pH-adjustment or dosages of phosphate-based inhibitors are measures in reducing copper corrosion. Especially phosphate in drinking water is believed to work as a corrosion inhibitor, but it is currently uncertain as to how this inhibitor works. In some cases the phosphate dosage aggravated the copper corrosion. The mechanisms are not yet clear and the influence of phosphate and pH remain a question to be answered. The results of a German Gas and Water Works Association (DVGW) research project on copper corrosion are presented as follows. The influence and the mechanisms of decarbonisation, deacidification and phosphate dosing on copper release in residential plumbing installations were studied in pipe rig experiments according to the German standard DIN 50931-1. It shows that an increased pH-value can lead to a decrease in copper content and that a phosphate dosage can lead to both higher and lower copper concentrations.

1 Introduction

For many decades copper has been proven as a material for residential drinking water installations. To date, copper and copper alloy pipes and fittings are used in approximately two thirds of all residential plumbing installations. This is due to their properties in the distribution of cold and warm water. The German drinking water standard limits the copper parameter to 2 mg/L [1]. This drinking water limit may not be exceeded at the fixtures for human consumption.

On the one hand, corrosion processes in residential copper installations can lead to leakages through pitting corrosion. Figures 1 and 2 show the typical appearances of a type one (cold water) pitting corrosion on a new copper installation system after only 1 year of operation. In this case, the damage was caused by the system not being fully emptied following a leakage test according to DIN EN 12502-1 [2]. This led to the stagnation of rest water. As a consequence the stagnated water prevented the build-up of a homogeneous and compact surface layer during the initialising phase. Beneath the corrosion pustules of the non-homogeneous surface layer, the copper pipes were attacked locally; respectively pitting corrosion took place and led to leakages.

On the other hand, corrosion processes in residential copper plumbing installations can increase the metal release in drinking water. If the copper limit for drinking water exceeds the 2 mg/L limit the drinking water can be treated to enable the use of copper material for residential installations. Central treatment steps such as pH-adjustment, softening/decarbonisation or phosphate-based inhibitors dosages are measures that can be applied to reduce the copper release.

There are only a few corrosion tests, which investigate the influence of treatment steps based on pH-change and phosphate dosages on copper corrosion. Especially phosphate is believed to work as a corrosion inhibitor in drinking water installations, but it is currently uncertain as to how this inhibitor acts. In context to a literature study of the influence of phosphate on copper corrosion in drinking water systems, it could be pointed out that a phosphate dosage can increase or decrease the drinking water copper content [3]. The mechanisms are not yet clear. Despite this uncertainty many water utilities use inhibitors to control copper corrosion [4].

In order to investigate the influence and mechanisms of pH and phosphate on copper corrosion in residential plumbing installations, various drinking waters were tested in different water works according to DIN 50931-1 [5].
2 Material and methods

2.1 Test waters

First, the influence of decarbonisation and phosphate dosage on copper corrosion was investigated. Corrosion tests according to DIN 50931-1 were performed in two different water works, test waters A and B. Each of the two water works operated with decarbonisation. Test water A is decarbonised by using Ca(OH)$_2$ (lime water), for test water B NaOH (sodium hydroxide) is applied. Furthermore, to examine the influence of orthophosphate on copper corrosion a particular flow of both test waters was spiked respectively with orthophosphate (sodium orthophosphate, Na$_2$HPO$_4$) to a phosphate concentration of 3 mg/L.

In order to determine the deacidification and phosphate dosage on copper release in drinking water systems further pipe rig experiments according to DIN 50931-1 were performed with test water C in a third water work. The pH-value of test water C was altered and three different pH-values resulted. Likewise, to examine the influence of orthophosphate on copper corrosion, a particular flow of the test waters (pH 7.1, 7.3 and 7.6) were spiked respectively with orthophosphate to a phosphate concentration of 3 mg/L.

The analysis of the test waters A and B prior to and following decarbonisation as well as the analyses of test water C are shown in Table 1. The results of the liquid chromatography analysis of the organic water components by means of liquid chromatography – organic carbon detection (LC-OCD) are shown in Table 2. It is to emphasise, that in comparison to the other analysed test waters, test water A prior to decarbonisation has the lowest concentration of humic substances.

| Table 1. Water quality parameter of test water A, B and C prior to and after treatment |

<table>
<thead>
<tr>
<th>Water A</th>
<th>Water B</th>
<th>Water C</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Decarbonisation</strong></td>
<td><strong>Decarbonisation</strong></td>
<td><strong>Deacidification</strong></td>
</tr>
<tr>
<td>Prior to</td>
<td>After</td>
<td>Prior to</td>
</tr>
<tr>
<td>pH</td>
<td>–</td>
<td>6.94</td>
</tr>
<tr>
<td>$r$ (pH)</td>
<td>°C</td>
<td>11.6</td>
</tr>
<tr>
<td>IOS</td>
<td>mmol/L</td>
<td>20.95</td>
</tr>
<tr>
<td>c(HCO$_3^-$)</td>
<td>mmol/L</td>
<td>7.71</td>
</tr>
<tr>
<td>c(CO$_2$) aq</td>
<td>mmol/L</td>
<td>2.12</td>
</tr>
<tr>
<td>c(Ca)</td>
<td>mmol/L</td>
<td>5.86</td>
</tr>
<tr>
<td>c(Mg)</td>
<td>mmol/L</td>
<td>0.86</td>
</tr>
<tr>
<td>c(K)</td>
<td>mmol/L</td>
<td>0.06</td>
</tr>
<tr>
<td>c(Na)</td>
<td>mmol/L</td>
<td>1.48</td>
</tr>
<tr>
<td>c(NO$_3^-$)</td>
<td>mmol/L</td>
<td>0.03</td>
</tr>
<tr>
<td>c(Cl)</td>
<td>mmol/L</td>
<td>2.57</td>
</tr>
<tr>
<td>c(SO$_4^{2-}$)</td>
<td>mmol/L</td>
<td>2.29</td>
</tr>
<tr>
<td>PI</td>
<td>mmol/L</td>
<td>3.67</td>
</tr>
<tr>
<td>$D_c$</td>
<td>mg/L</td>
<td>–34.5</td>
</tr>
<tr>
<td>c(O$_2$)</td>
<td>mg/L</td>
<td>8.8</td>
</tr>
<tr>
<td>TOC</td>
<td>mg/L</td>
<td>2.2</td>
</tr>
</tbody>
</table>

IOS, ionic strength; PI, buffer capacity; $D_c$, calcite saturation capacity; TOC, total organic carbon.

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2.2 Experimental set-up and evaluation according to DIN 50931-1

New hard drawn copper pipes of 5 m straight lengths and 13 mm internal diameters were used for the pipe rig experiments. These copper pipes are permitted for drinking water systems according to DVGW GW 392 [6]. All pipes originated from the same manufacturing batch with the product marking EN 1057 – R290 – 13 (Fig. 3 shows the pilot plant).

The copper pipes were then exposed to the test waters prior to and after the pH-change; respectively prior to and after the addition of 3 mg/L orthophosphate. In accordance to the standard DIN 50931-1 the test waters were then run through the test pipes for 1–2 min at a flow rate of 300 L/h. 22 flow cycles in turn with stagnation cycles ranging from 0.25 to 8 h, in total 145 L/day ran through each pipe. This flow and stagnation cycle is applied to simulate the family water consumption at a kitchen fixture.

Measurements were taken following 1, 2, 3, 6, 12, 18 and 26 weeks of operation. After 26 weeks the phosphate dosage for test water C (pH 7.1, 7.3 and 7.6) was discontinued. The test program was continued and a sampling was done another 2 weeks later (week 28).

The German standard also requires the sampling and evaluation in order to monitor the metal concentration in drinking water. For every measurement, eight stagnation samples are taken from each pipe following the stagnation cycles of \(2 \times 0.5, 2 \times 1, 2, 4, 8\) and \(16\) h. In accordance to this study the concentration of copper, dissolved oxygen and phosphate were measured in each sample.

The DIN 50931-1 states the following procedure for calculating the metal concentration in drinking water. Based on the concentrations, which were measured in the eight samples taken at the different stagnation times, an average metal concentration is evaluated called average copper concentration \(M(T)\)-value. As a result, each measurement has only one \(M(T)\)-value result for each pipe and accordingly for each water quality. The present, average copper concentration \(M(T)\) is the value used to determine the compliance of the German drinking water level according to the TrinkwV 2001 [1].

The DIN 50931-1 standard does not describe the procedure for evaluating the measured oxygen and phosphate concentrations. Therefore, the oxygen and phosphate consumption rates \(D_{O_2}\) and \(D_{PO_4}\) are established and explained as follows. The oxygen amount consumed by a copper pipe over the period of a complete day is called the oxygen consumption rate \(D_{O_2}\). According to DIN 50931-1, in each of the 22 stagnation periods the oxygen consumption is evaluated, determined and added. The oxygen consumption is \(D_{O_2}\) between the oxygen concentration prior to and after stagnation. Therefore the complete oxygen reduction during the cycle of 1 day is annualised in the unit \(\text{mol/}(m^2 \cdot \text{day})\), which represents the oxygen consumption rate \(D_{O_2}\). Consequently, for each measurement the test water only gets one oxygen consumption rate \(D_{O_2}\).

The phosphate consumption rate \(D_{PO_4}\) is determined by applying the same procedure as described above. It is based on the amount of phosphate in \(\text{mol/}(m^2 \cdot \text{day})\), which decreases due to the stagnation in the copper pipe. The content of phosphate prior to and following stagnation was measured, and the differences were estimated, respectively and then added up.

In addition to determining the copper, oxygen and phosphate concentrations the development and characteristics of corrosion scales were monitored. For this purpose copper pipe samples were taken during and after operation. The inner surfaces were analysed by scanning electron microscopy (SEM) and energy dispersive X-ray spectrometry (EDS).
3 Results and discussion

3.1 Influence of treatment steps on copper concentration

The average copper concentration $M(T)$ of the test waters A, B and C with and without the phosphate dosages versus operational times are represented in Fig. 4. Furthermore, the influence of the pH-changes and discontinuation of the phosphate dosages on test waters C are also demonstrated in Fig. 4c. An increase in the pH-value always resulted in a decrease in copper content. The phosphate dosage to all test waters resulted in different copper corrosion effects. The addition of 3 mg/L orthophosphate to test...
water A, prior to decarbonisation clearly increased the copper content (Fig. 4a). Whereas the same added phosphate dosage decreased the copper concentration in all other test waters.

Test water A, after decarbonisation, showed only low copper concentrations throughout the whole operational time. However, test water A prior to decarbonisation had a pH-value of 6.94 and a total organic carbon (TOC) concentration of 2.2 mg/L, which do not meet the DIN 50930-6 standard [7] for copper installations in residential drinking water installations. The average copper concentration $M(T)$ following 3 weeks of operation were always below the German drinking water limit of 2 mg/L (Fig. 4a, left), which in this case, questions the application of the DIN 50930, part 6. A phosphate dosage in this water increased the copper concentration, but during the operational time the values decreased (Fig. 4a). Following a further 26 weeks of operation, the average copper concentration was less than 2 mg/L.

The lower the pH-value of test water C the higher the copper concentration (Fig. 4c). The highest copper concentration with a pH-value of 7.1 was measured in test water C and this was without phosphate, the lowest pH-value of 7.6 was with phosphate. After discontinuing the phosphate additions to test water C, the copper concentration increased according to the pH-value.

### 3.2 Mechanisms of phosphate on copper corrosion

To explain the mechanisms of phosphate on copper corrosion in drinking water systems the sub-processes – oxygen reduction/copper oxidation and precipitation of a solid phase – have to be taken into consideration. With regard to this, it is to be noted, that the copper solid phase malachite ($\text{Cu}_2(\text{OH})_2\text{CO}_3$) in the corrosion system – drinking water/copper pipe – is the solid phase, which controls the copper solubility [8]. The corrosion of copper is a redox process. Through the reduction of the dissolved oxygen and the oxidation of the metallic copper, oxygen is consumed and copper goes into solution, respectively cupric ions ($\text{Cu}^{2+}$) are formed. Following the assumptions that the oxygen consumption was exclusively caused through the oxidation of the metallic copper to cupric ions; the oxygen consumption rate $\Delta O_2$ results strongly support the effect of phosphate mechanisms on copper corrosion.

Figure 5 shows the influence of a phosphate dosage on the oxygen consumption rates $\Delta O_2$ of test waters A, B and C (pH 7.1) versus the operation time. The development of the oxygen consumption rate $\Delta O_2$ of the test water C with pH-values of 7.3 and 7.6 is similar to the test water C with a pH-value of 7.1.

The results of Fig. 5 clearly show that an addition of phosphate decreased the oxygen consumption rate of all investigated test waters. This demonstrates the effect of phosphate on copper corrosion, which leads to lower copper release in drinking water. The less oxygen reduced during stagnation the fewer copper atoms are oxidised and the lower the copper concentration in water. Furthermore, the results of the oxygen consumption rate of test water C show that discontinuing the phosphate dosage increased the oxygen consumption rate. This in turn caused more copper to go into solution (Fig. 5c).

A phosphate dosage influences the precipitation of malachite and also the formation of a protective surface layer. A SEM-investigation of scale formation confirms that the phosphate dosage can hinder the precipitation of malachite. Figure 6 shows SEM images of corroded copper pipe surfaces, which were treated according to DIN 50931, part 1, with test water A prior to decarbonisation without phosphate (Fig. 6, left) and with phosphate (Fig. 6, right). The internal copper pipe surface of test water A (prior to carbonisation and without phosphate) was completely covered with malachite (Fig. 6, left). On the copper pipe surfaces of test water A (prior decarbonisation and with phosphate) resulting in higher copper concentrations in the water after stagnation no malachite was found (Fig. 6, right). The
internal pipe surface was coated by a brownish glimmering copper oxide layer (cuprites, \( \text{Cu}_2\text{O} \)).

In this case, the phosphate delayed the precipitation kinetics of malachite, so more copper stayed in solution. This effect of phosphate on copper corrosion increases the copper concentration of the water. The fact that phosphate can hinder the formation of malachite on copper pipe surfaces in drinking water installations has already been investigated and experimentally proven [8–10].

Potential reasons for the effects of phosphate on copper corrosion such as copper phosphate formations or calcium phosphate solids and sorption of phosphate ions on copper surface can be considered. This is discussed in more detail below. As a part of this research project it could be pointed out, that a phosphate dosage results neither in the formation of copper phosphate nor in the formation of calcium phosphate [11, 12].

Figure 7 shows the effect of orthophosphate on the solubility of copper in aqueous systems. The model calculations demonstrate that phosphate does not have any influence on cupric solvency, assuming that malachite is required to control the copper solubility in drinking water. These results have also been achieved in an United States Environment Protection Agency (USEPA) study [13].

X-ray photoelectron spectroscopy analysis of copper surfaces, which were treated with phosphate-spiked water and thermodynamic calculations support the assumption, that a solid calcium phosphate phase [hydroxyapatite (HAP)] precipitated on the copper surface. Figure 8 only represents the results of EDS on copper surfaces, which were run with test water C with a pH-value of 7.6. Similar results of EDS could be found on copper surfaces, which were treated with test waters A, B and C with pH-values of 7.1 and 7.3.

The comparison between the elemental scale constituents illustrates that on the copper surface, which was treated with phosphate-spiked water the elements calcium and phosphorus were found (Fig. 8, right). Without phosphate neither phosphorus nor calcium could be detected on the corroded surface (Fig. 8, left).

With regard to the EDS-spectra of Fig. 8, Fig. 9 describes the corresponding SEM-pictures of the copper surfaces. In comparison to the copper surfaces, which were exposed to the test water C without phosphate (Fig. 9, left) products of precipitated solids could be observed on copper surfaces, which were treated with phosphate-spiked water (Fig. 9, right). Considering that the structure of the calcium phosphate precipitation was amorphous and not crystalline. Also the copper surface was not completely covered by these amorphous products. Furthermore, it needs to be pointed out, that through analysing the copper surface by EDS (in contrast to Fig. 8, right), in some cases no calcium, but only phosphorus could be detected.

Model calculations for phosphate solubility confirm the results of the surface analysis of corroded copper pipes. In comparison to the solid copper phosphate phase, the calcium phosphate is the solid phase which controls the phosphate solubility in drinking water or rather in the test waters (Fig. 10).

Not only the amorphous structure of the calcium phosphate phase and the incomplete covering of the copper surface, but also the results of a study [9] support some doubts on the assumption that calcium phosphate precipitates and forms a protective layer on the internal copper pipe surface. In pipe rig experiments according to DIN 50931-1 with synthetic waters (without calcium) it was observed that in the presence of dissolved organic carbon (DOC) phosphate decreased the copper release, whereas without...
applying DOC there were higher copper concentrations with phosphate dosages [9].

It can be assumed that the formation of calcium phosphate on the inner copper pipe surface is more than likely a side-effect. By exceeding the solubility product, amorphous structures precipitate and do not cover the surface completely.

The evaluation of the phosphate measurements indicates the adsorption of phosphate ions on the copper surface. In Fig. 11, the phosphate consumption rate $\Delta P_{O_4}$ of test waters A, B and C are presented versus the operation time according to the pH-values. During the first few weeks of operation, the $\Delta P_{O_4}$ increased according to the pH-value. The higher the pH-values the more phosphate was consumed and remained on the pipe. Then the phosphate consumption rate decreased in the course of the operational time, which was based on the pH-value. The higher the pH-values the more phosphate was consumed and remained on the pipe. By the end of the corrosion tests, almost no phosphate was consumed. So following the stagnation period of 16 h the initial dosage concentration of 3 mg/L had only decreased minimally.

The results of the phosphate mass balance promote the idea that phosphate adsorbs on copper surfaces in drinking water installations and eliminates the continual formation of calcium phosphate. If the solubility and the precipitation of calcium phosphate were the dominant effects of the phosphate dosage, then the phosphate concentration had to be reduced continuously.
and constantly during stagnation. Obviously, this is not the case. So it can be assumed that the adsorption of phosphate ions on the copper surface blocks the active sites.

Blocking the active sites on the surface can protect metallic copper against oxidation, but can cause less copper ions being transferred into the aqueous phase, respectively the copper release on the stagnated water is decreased. Blocking the active sites on the copper surface can also kinetically hinder the crystallisation of cupric ions, which can inhibit the precipitation of malachite on the copper surface. More copper stays in solution and the copper concentration in the stagnated water increases. As a consequence, orthophosphate can decrease or increase the copper release, depending on which of the two effects is dominating. Further investigations are being carried out to verify the phosphate adsorption on the copper pipe surface.

3.3 When does phosphate increase copper release?

The results of these corrosion tests and a literature study [3] show that a phosphate dosage only increased the copper concentration in drinking waters with pH-values ≤7.4, which already shows that without phosphate there is only a low copper release during stagnation. Furthermore, it could be proven, that the natural organic matter concentration and composition (TOC) influences the phosphate action mode on copper corrosion. Humic substances can also hinder the precipitation kinetics of malachite in aquatic systems, so more copper stays in solution and the copper concentration increases [12].

If the TOC has almost no influence on the crystallisation velocity of malachite – and malachite can precipitate fast – the results are low copper concentrations. Also the effect of phosphate on copper corrosion dominates, which decreases the oxygen reduction, respectively the copper oxidation. A phosphate dosage can then result in lower copper concentrations in the stagnated water.

3.4 When does phosphate decrease copper release?

Due to the precipitation of malachite being hindered through the absorption of humic substances on the inner copper pipe surface, there was an increase in the copper concentrations. The effect of phosphate on copper corrosion dominates, which decreased the oxygen reduction, respectively the copper oxidation. A phosphate dosage can then result in lower copper concentrations in the stagnated water.

3.5 Mechanisms of pH-adjustment

As shown in Fig. 12, a pH-value increase in all test waters resulted in a decrease in the oxygen consumption rate \( \Delta O_2 \). Consequently less copper was oxidised and resulted in solution. One possibility is due to the higher pH-value of the drinking water or the lower solubility of malachite. As a result of increasing the pH-value, more compact surface layers can be built up on the inner copper pipe surface. Due to the lower copper solubility, which supports the formation of a more compact surface layer, the copper surface is now protected against the corrosive attack of the dissolved oxygen. Furthermore, the velocity of the reduced oxygen, respectively the copper oxidation decreases, resulting in less copper going into

![Phosphate consumption rate \( \Delta P_{O_4} \) based on operation time and on pH-value. (a) Water A; (b) water B; (c) water C](image-url)
solution. It should be noted that the malachite layer on the copper surface also acts as a ‘copper swale’. The corrosion reaction causes cupric ions to go into solution. An increase in the pH-value lowers the copper solubility and results in the formation of more compact and protective surface layers. As a consequence, extensions and modifications to water treatment systems in which the pH-value is increased through decarbonisation or intensification of the aeration can also be seen as corrosion protective measures against copper corrosion in residential drinking water installations.

The 3 mg/L orthophosphate dosage could both increase and decrease the copper release during stagnation. Based on copper pipe surface analysis samples and solubility calculation results from the pipe rig experiments, it can be assumed that phosphate ions adsorb and block the active sites on the inner copper pipe surface. With regard to this, two mechanisms on the influence of orthophosphate on copper corrosion in drinking water systems could be pointed out. On the one hand a dosage of orthophosphate reduced the oxygen consumption, causing less copper to go into solution. On the other hand a dosage of phosphate hindered the precipitation of the copper solid phase malachite. So more copper stayed in solution and the copper concentration of the water increased. As a consequence, phosphate dosing can increase or decrease the copper corrosion, and this depends on which of the two effects is more dominating. The dominating effect depends on the concentration and the composition of the dissolved organic matter such as humic substances.

Based on these results and on copper concentration measurements, it can be estimated whether a phosphate dosage decreases or increases the copper release in drinking water systems: if only low copper concentrations are measured in the drinking water without phosphate, which is presumably due to the formation of malachite on the pipe surface, an addition of phosphate can increase the copper concentration in which it hinders the precipitation of malachite. If high concentrations of copper are measured in the stagnation water, the effect of phosphate on copper corrosion dominates, which reduces the copper oxidation and thus reduces copper release into the drinking water.

Finally it is to be noted that a dominating sorption effect of phosphate ions on the copper surface can enable water utilities to reduce phosphate dosage to a minimum, which would significantly reduce operational costs. With regard to this, further investigations are necessary.

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5 References


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