Electrochemical testing of different corrosion inhibitors and their effect on copper pitting corrosion in drinking water

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Summary

The application of phosphate- and/or silicate-based corrosion inhibitors is a widely used method to counteract on corrosion problems in drinking water distribution systems. In this study the efficiency of some commercially available corrosion inhibitors against copper pitting corrosion was investigated. The tested inhibitors consisted of different mixtures of phosphates (varying contents of ortho- and poly-phosphate) and activated silicates. Their effect on the pitting corrosion behaviour of copper pipes was tested electrochemically in batch experiments. These tests were complemented by surface analysis, especially pit morphology.

The electrochemical method applied was galvanodynamic polarisation of a copper pipe half-shell immersed in the water of interest where the respective inhibitor was dosed. The polarisation was conducted in anodic and in cathodic direction so that the two corresponding basic corrosion reactions could be examined separately. The results revealed a characteristic run of the anodic current potential curves which show a region of repassivatable pitting, a passive area and a region of active pitting corrosion. The use of corrosion inhibitors can shift the values of the pitting potential to more positive or more negative values, depending on the concentration of the inhibitor and its composition. The cathodic current potential curves show an area where the limiting current of the oxygen diffusion can be determined. Its value describes the cathodic activity of the corrosion system and is also an indicator of the effectiveness of the applied corrosion inhibitor.

The results show that the test method applied here is suitable for rapid testing, e.g. for identifying the available corrosion inhibitors to be shortlisted for further detailed examination in a given drinking water.

1   Introduction

The corrosion of copper pipes in drinking water is a process of electrochemical nature where the copper pipe acts as a heterogeneous (active/passive) electrode in water electrolyte. Therefore the process can be divided into an anodic and a cathodic reaction.

The anodic reaction of metal oxidation may lead to pitting corrosion and occurs at defect spots within the copper oxide passive layer. It follows equation (1)

$$2\,Cu \rightarrow 2\,Cu^{2+} + 4\,e^- \qquad\qquad (1)$$

At the cathode the oxygen dissolved in the water is reduced (equation (2)):

$$O_2 + 2\,H_2O + 4\,e^- \rightarrow 4\,OH^- \qquad\qquad (2)$$
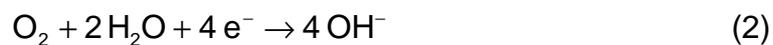
It has to be considered that also the water constituents take part in these reactions, for example calcium ions and hydrogen carbonate ions.

The resulting secondary reaction at the anode is the formation of malachite (equation (3)):

$$2\,Cu^{2+} + HCO_3^- + 3\,OH^- \rightarrow Cu_2(OH)_2CO_3 \downarrow + H_2O \qquad\qquad (3)$$
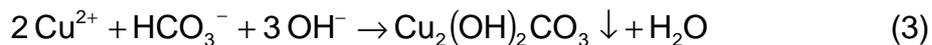
The resulting secondary reaction at the cathode is the formation of calcium carbonate (equation (4)):

$$HCO_3^- + OH^- + Ca^{2+} \rightarrow CaCO_3 \downarrow + H_2O \qquad\qquad (4)$$
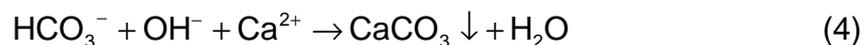
These reactions lead to the formation of a surface layer inside the pipe, where the precipitation of malachite as well as the formation of calcium carbonate result in a secondary salt layer passivation of the system [1; 2; 3].

When speaking of copper pitting corrosion one has to consider different types. This paper will focus on type I, which only occurs in cold drinking water. The other types are type II in hot drinking water, type III as a modification of type I, occurring in very soft drinking waters and microbially influenced corrosion (MIC).

1.1   Copper pitting corrosion type I

Pitting corrosion of copper pipes in drinking water installations is a system of multiple factors. It is affected by the material itself (manufacturing and processing), the operating conditions of the installation and the water composition [1; 2; 3].

- *Influence of the material:* Defects in the primary oxide layer on the inside wall of the pipe, inhomogeneities or the formation of copper(II) oxide layers by extreme heat treatment (for example hard soldering) cause a susceptibility to local attacks. Therefore the condition of the material influences the initiation process of pitting.

- *Influence of the operating conditions:* Long stagnation periods of the water in the pipe and laminar flow conditions promote a stabilisation of local elements on the surface. This is due to the lack of transport of corrosion products. This influence mainly affects the initial phase of pitting at the anode.
  The delivery of oxygen to the cathode by the typical flowing conditions during usual service of the installation affects the stabilisation and the progress of the corrosion process.

- *Influence of the water composition:* The anodic part of the pitting process represents the initiation of pitting and pit growth. It is mainly influenced by the interaction of the anions sulphate (promoting), nitrate (promoting), chloride (inhibiting) and hydrogen carbonate (buffering). Here the ratios of these anions towards each other are more crucial than their individual concentrations.
  The cathodic part of the pitting process is influenced by the calcite precipitation and organic trace elements, which lead to a blocking of the semi-conducting properties of the oxide layer and thereby to an inhibition of the cathodic reaction.

Considering the factors mentioned above, it has to be emphasised that pitting corrosion can only occur in the coincidence of critical factors [1].

1.2 Corrosion inhibitors in drinking water

The use of corrosion inhibitors for corrosion protection in drinking water is a common, well used method but it is necessary to pay attention to the mechanisms due to the different materials coexisting in a water supply network including the drinking water installation.

Drinking water treatment with corrosion inhibitors based on phosphates or activated silicates is a common method to avoid corrosion problems with "red water" or discolouration in water distribution networks with a high amount of old cast iron pipes [4]. Inhibitors are also used to minimise copper and lead concentration in drinking water if the solubility of copper or lead with respect to the drinking water characteristics is high. In some cases inhibitors are used successfully to minimise problems with pitting corrosion of copper but in general there are no accompanying investigations so that there are no reliable data of the effectiveness.

Due to the German drinking water directive and based on the German technical rules it has to be mentioned that the application of corrosion inhibitors should only be considered if other water treatment processes are either not possible or if their application is not successful in terms of corrosion inhibition [5].

When speaking of corrosion inhibitors it has to be distinguished between *anodic inhibitors* which inhibit the anodic corrosion reaction, *cathodic inhibitors* which inhibit the cathodic reaction and *anodic/cathodic inhibitors* which inhibit both reactions. Anodic inhibitors are also called *dangerous inhibitors* because if there are surface areas where the concentration of the inhibitor is too low these areas become very active local anodes [1].

In drinking water applications in Germany only inhibitors based on phosphate- and/ or activated silicate can be used according to the German drinking water directive [6].

The following list gives an overview of the main effects on copper corrosion according to German technical rules [5; 7].

- *Phosphate-based inhibitors* can be composed of orthophosphates, polyphosphates or mixtures of both. Orthophosphates are salts of phosphoric acid where the hydrogen ions are substituted by metal ions like sodium, potassium or calcium. They promote the formation of protecting surface layers in copper pipes and thereby inhibit general corrosion and by-product release. Polyphosphates originate from hydrogen phosphate by intermolecular dehydration and formation of P-O-P bonds. For the application as corrosion inhibitors in drinking water long chained polyphosphates with chain length between 10 and 30 are preferred. Polyphosphates promote general corrosion in copper pipes instead of inhibition. They are rather applied for masking of iron and/or manganese in iron-based pipes. Their only inhibiting effect is the conversion to orthophosphate by hydrolysis [5]. The limiting value for phosphates in drinking water according to the German drinking water directive is 6.7 mg/l [6].

- *Inhibitors based on activated silicates* can be composed of sodium silicate mixed with sodium hydroxide, sodium carbonate or sodium hydrogen carbonate. In iron-based pipes the application of this kind of inhibitor leads to the formation of stable surface layers which inhibit further corrosion. Compared to that there are no generally accepted findings about the effect of activated silicates on the corrosion of copper. [7]. The limiting value for silicates in drinking water according to the German drinking water directive is 15 mg/l [6].

- Mixtures of phosphates and activated silicates have similar effects on corrosion as phosphate-based inhibitors. In addition, there can be synergetic effects [7]. In certain cases it can be possible to optimise the application of the inhibitor by a stepwise substitution of the phosphate component by the activated silicate component [4].

Here it has to be mentioned that the inhibitory effects described above are only valid for general corrosion of copper. Studies about the effect of corrosion inhibitors on general corrosion of copper pipes in test rigs under conditions similar to those in real domestic installations have shown that all inhibitors tested there reduced the cuprosolvency significantly. It was found out that the phosphate-based inhibitors stabilised the surface layers by the formation of poorly soluble compounds while the activated silicates built up thin films on top of the surface layers [8].

The effects of these inhibitors on pitting corrosion of copper have also been investigated but the findings of such investigations did not lead to generally accepted statements yet. This is due to the fact that most studies on inhibitors and copper pitting corrosion have not been conducted systematically in drinking waters. Many statements found in literature are based on case studies of rehabilitation measures where inhibitors have been applied to copper installations damaged by pitting corrosion [1]. As it is difficult to formulate certain mechanisms for the effectiveness of corrosion inhibitors on copper corrosion in general, it is even more difficult to do so for the special case of pitting corrosion of copper. This is due to the fact that the process of pitting corrosion and the factors influencing it (especially the role of water composition) is still not fully understood. Therefore it is extremely challenging to

initiate and stabilise copper pitting corrosion under defined experimental conditions which would be necessary to investigate the effects of corrosion inhibitors systematically [1].

Some of the most interesting statements on the effect of corrosion inhibitors on the pitting corrosion of copper are listed below with the limitation that these statements cannot be seen as generally accepted due to the reasons mentioned above:

- Pure polyphosphates can support pitting corrosion in old copper pipes by accelerating general corrosion and thereby reactivating repassivated anodes [9]. This can be positive in new pipes as local processes can not stabilise due to the high rate of general corrosion [10].
- Orthophosphates and combination products with orthophosphate as the main component seem to inhibit pitting corrosion of copper [1; 11; 12; 13; 14].
- Products based on activated silicates can promote pitting corrosion of copper under unfavourable conditions [1; 3; 13; 14; 15].

1.3 Aim of this study

The investigations presented here have been conducted to find a method suitable for rapid testing of the pitting corrosion behaviour of copper in drinking water under varying conditions. In this study the conditions were varied by adding different corrosion inhibitors to the test water.

As explained above it is difficult to initiate and stabilise copper pitting corrosion under defined experimental conditions on the one hand, and to predict the effects of corrosion inhibitors on these processes on the other hand. Investigations of this kind normally consist of long-term tests with exposure of copper specimens or pipes to the respective water with and without the inhibitor. As these investigations can be very expensive due to their duration, it seems necessary to have a method for rapid testing.

Even though most rapid tests are said to be not very accurate or that their results might not be valid for the long-term behaviour, such rapid tests can aid in the planning phase of detailed long-term tests, for example by the identification of the available corrosion inhibitors to be shortlisted.

2 Experiments

As expressed in the introduction, the corrosion processes of copper in drinking water are of electrochemical nature. Therefore electrochemical methods can be applied to investigate the effects of different corrosion inhibitors on the pitting corrosion of copper in drinking water.

The method applied here was a modification of a method for the determination of pitting potentials of stainless steel samples exposed to water [9].

2.1 Sample preparation

The copper samples used in these investigations were made of commercially available copper tubes with 22 mm diameter. Pieces of 4 cm length were cut into half shells. At the shorter side of the respective sample a hole of 2 mm diameter was drilled where a copper wire was fixed by twisting. This was done to be able to immerse the sample in a beaker filled with the test water and to have an electrical connection to the measuring instrument during the experiment.

The samples were degreased in acetone, pickled for 15 seconds in 10% nitric acid, rinsed with deionised water and dried with oil-free pressurised air. This was done to have similar and comparable surface conditions for all experiments.

After that a special sample mask sticker was fixed to the sample so that only a defined area (3.14 cm²) of the inner surface was exposed to the water in the following experiments. The other reason for the application of these stickers was the avoidance of edge effects. A sample prepared in this way is shown in Figure 1.
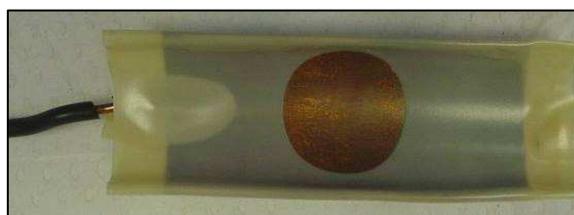
Figure 1: A copper sample after preparation with copper wire (left) and special sample mask sticker

2.2 Experimental setup

In all experiments described here a double-walled beaker was used. Its lid had several holes to hold the electrodes needed for the tests.

According to the classical three-electrode-setup there was the copper sample as the working electrode where the current is applied for the experiment, a reference electrode (Ag/AgCl) to measure the potential and a platinum sheet serving as the counter electrode to close the electrical circuit.

The copper sample was placed in a special sample holder with the help of the attached copper wire so that it hung freely in the sample solution. The other electrodes were also fixed to the beaker lid so that all of them were able to be immersed in the sample solution. This solution was stirred with a magnetic stirrer and aerated with oil-free pressuirised air via a glass frit. This was done to maintain a similar and comparable oxygen saturation of the water in all experiments.

The whole experimental setup was placed in a Faraday steel cage to avoid stray signals from outside during the polarisation experiments.

The temperature of the water was kept constant at 25℃ by pumping tempered water through the double jacket of the beaker. Figure 2 shows a schematic overview of the experimental setup.
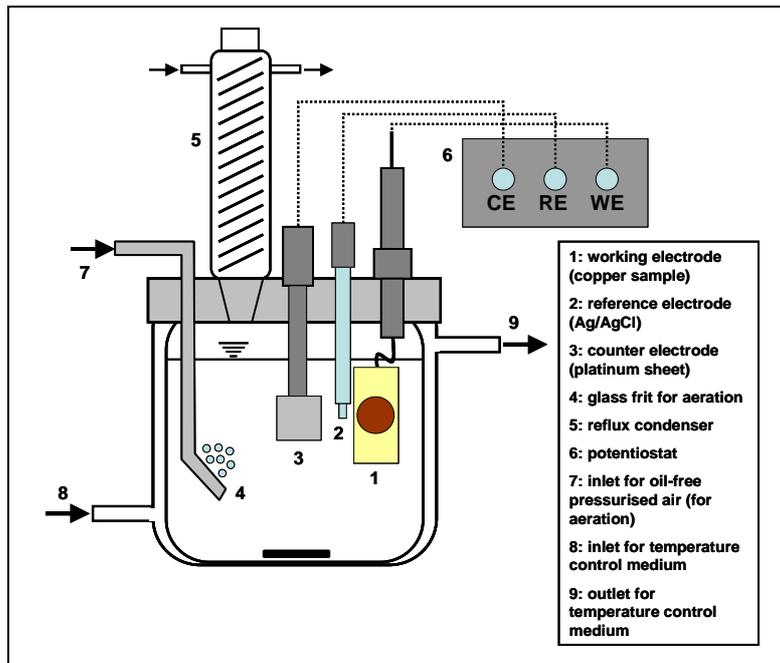
Figure 2: schematic overview of the experimental setup

2.3 Procedure of the experiments

For all experiments described here the beakers were filled with 500 ml of the respective test solution.

All electrodes (including the respective copper sample as working electrode) were fixed to the beaker lid and thereby immersed in the test solution. The electrodes were connected to the potentiostat (Reference 600, Gamry).
First the free corrosion potential was measured for one hour. This is the potential signal of the sample immersed in the water without any outer disturbance. After one hour this free corrosion potential was nearly constant so that the polarisation tests could be started (with the same sample).

The method applied here was the galvanodynamic polarisation. That means that a small current was applied to the copper sample and the resulting potential was measured. The applied current was slightly increasing with a rate of 1 nA/cm²*s during the anodic polarisation test for a duration of 69 hours.

In the cathodic polarisation tests the applied current was decreasing at the same rate and each experiment lasted 48 hours. For every single polarisation test decribed here a new copper sample was prepared according to the procedure described above. This was done to have comparable starting conditions for each experiment.

All experiments described here were performed by testing the two half-shells of a pipe section in two identical beakers with identical setup simultaneously as repeat determination.

2.4 Composition of the water and the inhibitors tested

The test water was a natural drinking water and was taken from a water works in western Germany. It was a mixture of a hard groundwater rich of neutral salts and

the same water treated by nanofiltration to reduce hardness and anion content. A list of the most important parameters is given in Table 1:

Table 1: List of the most important parameters of the tested water

parameter and dimension		value
pH	-	7.7
conductivity	µS/cm	440
total hardness	°dH	11
total hardness	mmol/l	1.9
total hardness	ppm $CaCO_3$	195.8
acid capacity (HCO_3^-)	mmol/l	2.8
acid capacity	ppm $CaCO_3$	140
chloride	mg/l	16
sulphate	mg/l	50
Nitrate	mg/l	12

Based on practical experience, this water is known to be able to support pitting corrosion of copper. This is a little bit astonishing because the corrosion characteristics of the water composition do not represent those expected for a water that supports pitting corrosion.

For each experiment a fresh water sample was taken to avoid alterations of the water composition due to long storage periods.

The corrosion inhibitors applied here were ready-to-use liquid products provided by BK Giulini GmbH, Ludwigshafen, Germany. The products and concentrations were chosen according to practical experience with copper general corrosion, e.g. minimising the copper concentration in the water to comply with the drinking water directive. Table 2 shows a list of these corrosion inhibitors and the respective concentrations used in the investigations described here.

Table 2: List of corrosion inhibitors tested

composition	concentration
ortho-/polyphosphate 70/30	4 mg/l total PO_4^{3-}
ortho-/polyphosphate 70/30	2 mg/l total PO_4^{3-}
ortho-/polyphosphate 70/30 + carbonate-activated sodium silicate	2 mg/l total PO_4^{3-} + 2 mg/l SiO_2
ortho-/polyphosphate 100/0	2 mg/l total PO_4^{3-}
ortho-/polyphosphate 0/100	2 mg/l total PO_4^{3-}
carbonate-activated sodium silicate	2 mg/l SiO_2

The test solutions were prepared by adding a certain volume of the respective inhibitor to the water sample to achieve the desired inhibitor concentration.

3 Results

3.1 Galvanodynamic polarisation in anodic direction

The galvanodynamic polarisation experiments resulted in characteristic current-potential curves. One representative curve is shown in Figure 3 to illustrate the meaning of the different regions in the run of the curve and to demonstrate how the pitting potential was determined as this was the main criterion for the evaluation of the experiments. In the diagram the current (in µA) is plotted against the potential (in mV vs. an Ag/AgCl electrode).
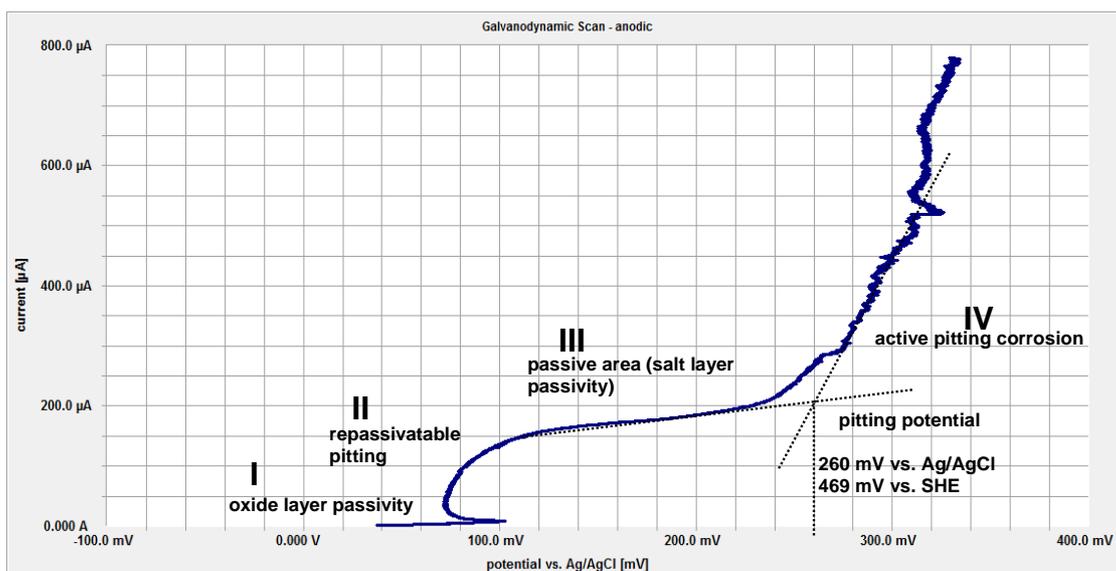
Figure 3: Example of a galvanodynamic polarisation curve in anodic direction with the significant regions; the method of estimating the pitting potential is indicated by the dashed lines

The significant regions in the run of the curve can be described as follows:

First there is the plateau which indicates the oxide layer passivity of the sample (region I).This oxide layer was already formed during the production process of the tube. As described above, each sample was pickled before the respective experiment. But the pickling did not remove the oxide layer because it was just intended to clean the uppermost layer of the surface to have comparable starting conditions for each experiment.

After that the curve rises, which can be seen as repassivatable pitting (region II).

This is followed by another plateau which represents a passive area (salt layer passivity; region III), where malachite is precipitating.

When the curve rises again, there is the region of active pitting corrosion (region IV):

The pitting potential was estimated by drawing a straight line on the slope of the passive region and another straight line on the slope of the active region. The intersection of these lines (shown as dashed lines) yields the pitting potential. By this method both the passive and the active portion of the curve are taken into consideration As the investigations described here were conducted as comparison

tests, this evaluation method has shown to be a proper tool for the comparison of the results of the experiments.

The pitting potentials derived from the anodic polarisation curves are shown in Figure 4 to compare the effects of the inhibitors.
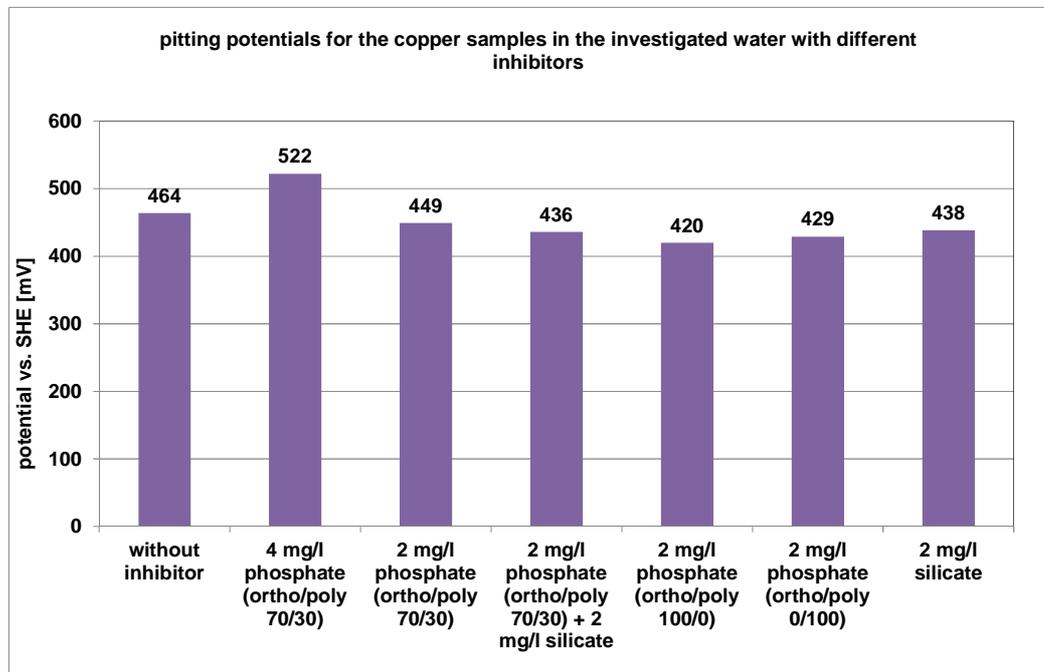
Figure 4: Pitting potentials of the copper samples in the investigated water with different inhibitors

The results in Figure 4 show a certain trend. The pitting potential of the water without inhibitor can be seen as the reference for these investigations in the given water. It is obvious that the addition of 4 mg/l of the inhibitor with 70% ortho- and 30% polyphosphate shifts the pitting potential to significantly higher values and therefore seems to inhibit pitting corrosion. Adding the same inhibitor in a reduced concentration of 2 mg/l leads to a lower pitting potential which is approximately in the same order of magnitude as for the water without inhibitor. The other inhibitors tested here led to pitting potentials with slightly more negative values. If a ranking would be set up here, the inhibitors with pure ortho- and pure polyphosphate would be less efficient.

3.2 Galvanodynamic polarisation in cathodic direction

As described in the introduction, a corrosion process always consists of anodic and cathodic reactions. Therefore the results for galvanodynamic polarisation in cathodic direction also have to be taken into account. In those diagrams the current is plotted against the potential. The resulting curves show a certain run with a significant plateau phase. This plateau shows the oxygen diffusion limiting current which is an indicator of the intensity of the cathodic part of the corrosion reaction. The higher the value of this current, the more intense is the corrosion reaction.

Here it has to be mentioned that the current values in the diagram are expressed as negative numbers. As negative currents do not exist, the signs of these numbers

have to be switched to positive for the evaluation. The diagram in Figure 5 shows an example of such a curve.
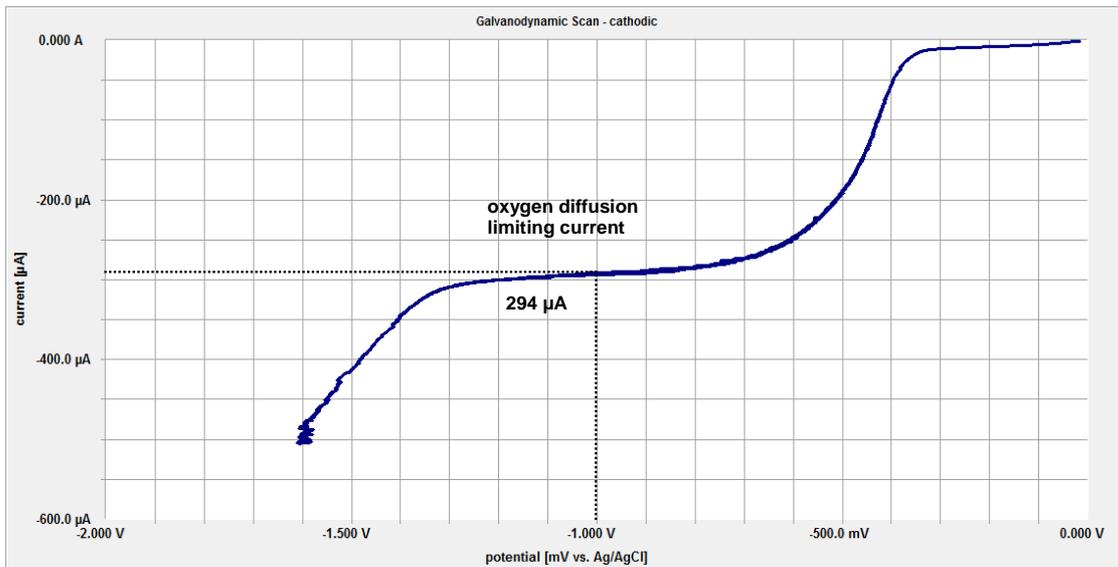
Figure 5: Example of a galvanodynamic polarisation curve in cathodic direction with the significant plateau phase indicating the limiting current of oxygen diffusion

For the estimation of the oxygen diffusion limiting current the current value at a potential of -1.0 V was read. This was done to be comparable because the center of the plateau of almost all cathodic curves was situated around this potential value. It has to be expressed that the results obtained with this evaluation method do not deliver absolute values, but a comparison under identical conditions.

Similar to the pitting potentials the oxygen diffusion limiting currents of all experiments are shown in the following diagram (Figure 6).
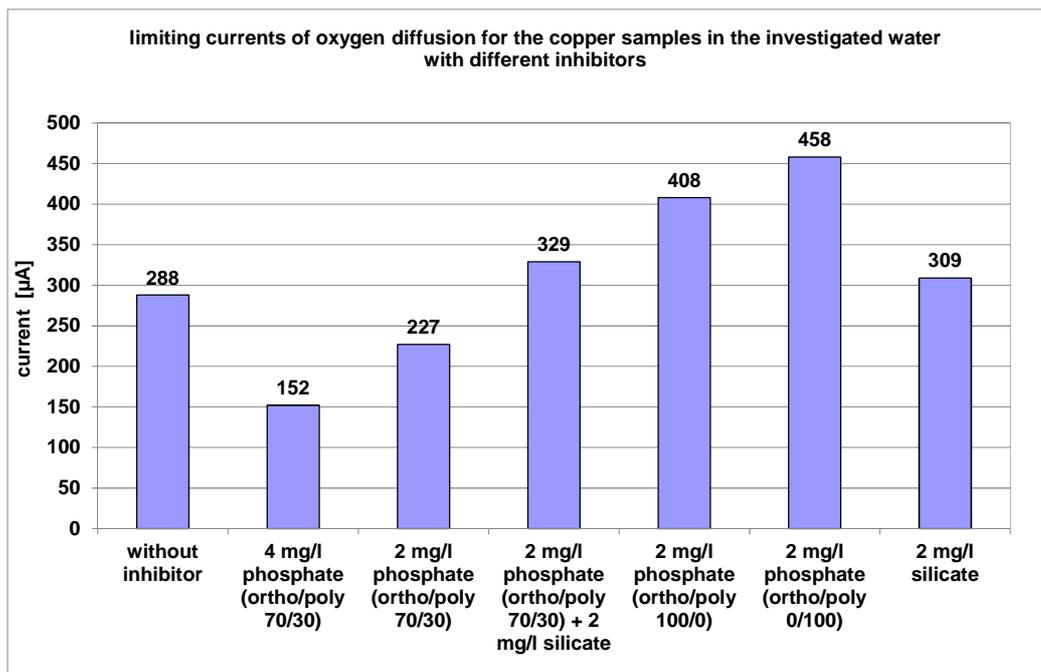
Figure 6: Oxygen diffusion limiting currents of the copper samples in the investigated water with different inhibitors

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The results show that here also the inhibitor with a mixture of 70% ortho- and 30% polyphosphate has the best inhibitory effect compared to the current value for the samples in the non-inhibited water. This holds for both concentrations tested here. All other inhibitors show higher values for the oxygen diffusion limiting current, especially the products with pure ortho- and pure polyphosphate.

3.3 Surface analysis

To complete the investigations described above, also the surfaces of the copper samples were investigated after the respective experiments. This was done by a photographic documentation of the surfaces, pickling and investigating the pit depths.

3.3.1 Surfaces of copper samples after anodic polarisation

All copper samples showed voluminous greenish corrosion products after anodic polarisation. These products are mostly basic copper salts like malachite, for example. They were loosely attached to the surface so that it was unavoidable that some parts of the surface layer were detached just by the movement of the sample when pulling it out of the water after the respective experiment. Therefore a quantitative analysis of the surface layers was not possible here.

In the following the surface analysis conducted in this study is described by showing the results for some representative samples. These samples had been exposed to

- the test water without inhibitor
- the test water with the mixture of ortho- and polyphosphate in the concentration of 4 mg/l
- the test water with the phosphate/silicate mixture.

A collection of some of the surfaces after anodic polarisation can be seen in Figure 7.

| without inhibitor | with 4 mg/l phosphate (ortho/poly 70/30) | with 2 mg/l phosphate (ortho/poly 70/30) + 2 mg/l silicate |
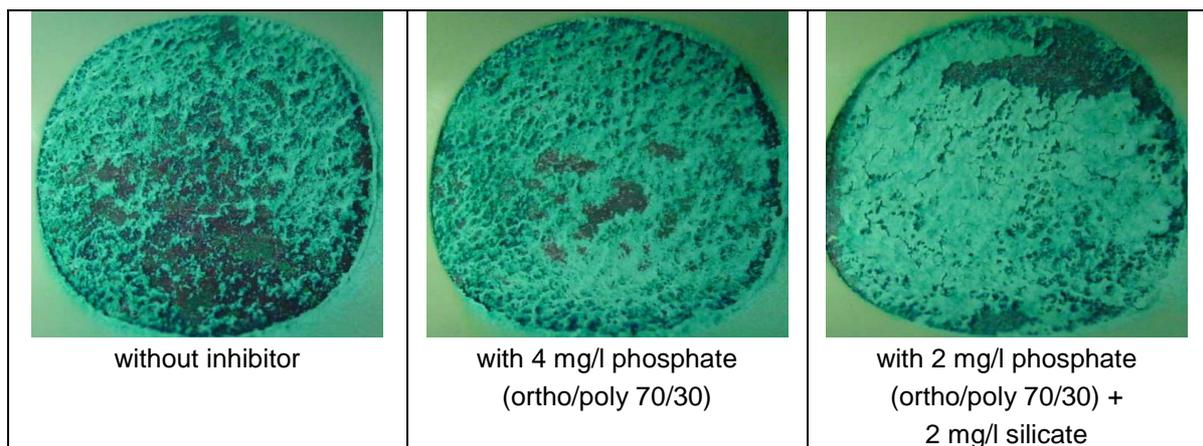
Figure 7: copper samples after anodic polarisation with loosely attached corrosion products

Looking at the photos in Figure 7 it is quite visible that parts of the surface layer are missing as described above. And it can be stated that the layer of the sample after exposure to the water with the phosphate/silicate inhibitor shows a slightly different structure than the others as it looks more like a layer than like single spots of

corrosion products. This is due to the silicate component of the inhibitor which is known to form layers instead of incorporating into existing corrosion products. But, as described above, the corrosion products of all samples in these investigations were very loosely attached. This can be attributed to the electrochemical method applied as it accelerates the corrosion reaction in a way that the corrosion products do not have the time to properly adhere to the material's surface.

As the next step the samples were pickled in 10% nitric acid for 90 seconds to completely remove the surface layer. After that the bare copper surface was visible including some local attacks which had to be examined under the microscope. Macroscopic pictures of the pickled surfaces as well as some details (200fold magnification) are shown in Figure 8 and 9.

| without inhibitor | with 4 mg/l phosphate (ortho/poly 70/30) | with 2 mg/l phosphate (ortho/poly 70/30) + 2 mg/l silicate |
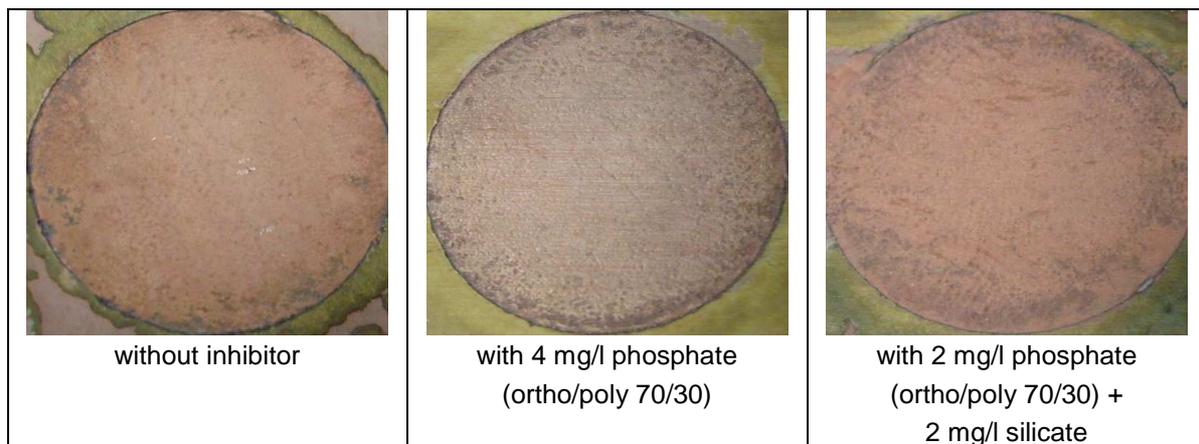
Figure 8: copper samples after anodic polarisation and after pickling

The samples which were exposed to the water with inhibitor (Figure 8, middle and right) show a relatively rough surface while the surface of the sample exposed to the non-inhibited water seems to be relatively smooth. All samples show a more or less rough surface structure caused by local attacks.

For a more detailed analysis the surfaces were examined under the microscope with 200fold magnification. The depth of some of the pits was determined by optical focussing. That means that first the focus was set on the edge of the respective pit and then on the bottom of it. Thereby the height of the ocular of the microscope was changed. This change of height was measured with a fine instrument attached to the microscope and gained the depth of the pit in µm. Figure 9 shows microscopic photos of the deepest pits of the investigated samples and schematic illustrations of the respective pit profiles.
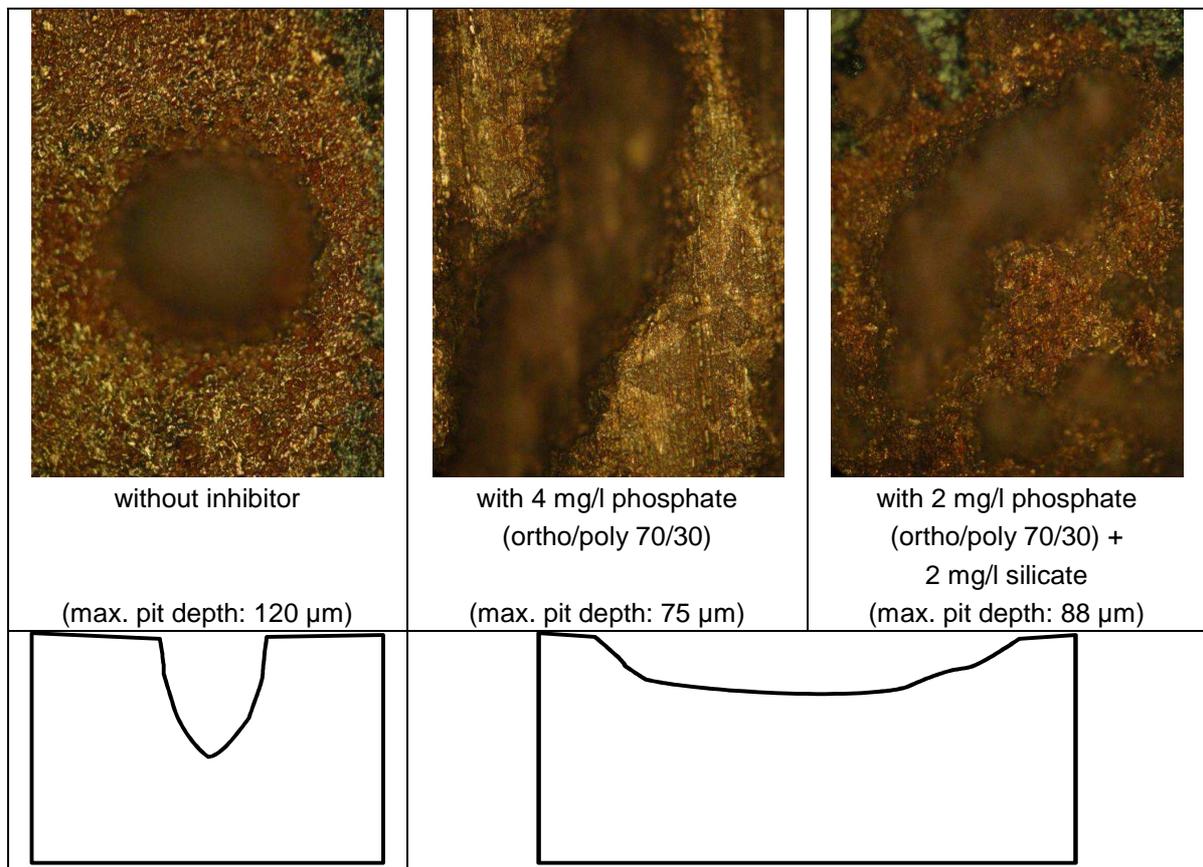
Figure 9: microscopic (200fold) view of local attacks on the surfaces of the copper samples and schematic illustrations of the respective pit profiles

The pits found on the surface of the copper sample which was exposed to the water without inhibitor show the typical shape of type I pitting corrosion. They are relatively narrow and circular. The deepest one was found to be 120 µm deep. Most of the others were micropits with depths ranging from 20 to 65 µm. Their number on the surface of this sample was estimated to be several hundreds of pits.

The total numbers of pits on the surfaces of the other samples were in the same order of magnitude but their morphology was different. The sample which was exposed to the water with the mixed phosphate inhibitor showed very wide and shallow pits with a maximum depth of 75 µm. It seems as if the inhibitor had an influence on the shape and depth of the pits. The sample which was exposed to the water with the mixed phosphate/silicate inhibitor showed both types of pits with the majority being also wide and shallow. The deepest one was 88 µm.

The results show that pitting corrosion occurred on all samples, independend of the dosage of an inhibitor to the test water. To understand this, one has to consider the method applied here. Galvanodynamic polarisation in anodic direction means that a steadily increasing current is applied to the copper sample so that it is forced to corrode until the passive layer breaks down and pitting is initiated. This can be seen by the steep rising of the polarization curves (region IV in Figure 3). So the criterion for the comparison of the different experiments is the position of the pitting potential on the one hand, and the pit morphology on the other hand.

The most interesting finding here is that the pits in the samples exposed to the test water without inhibitor showed the typical morphology of pitting corrosion type I, while those in the samples exposed to the water with inhibitor have the appearance of shallow pits. These shallow pits are normally formed by many smaller pits which grow together. That means that the number of pits is increasing, but not their depth. In this case one can also speak of repassivating pitting corrosion.

3.3.2 Surfaces of copper samples after cathodic polarisation

The copper samples after cathodic polarisation showed no significant alteration of their surface. The only exception was the sample which was exposed to the water without inhibitor. Here some white crystalline products were found. It can be suggested that these products are mainly calcite precipitates. A small selection of surfaces is shown in the next set of photos (Figure 10).

| without inhibitor | with 4 mg/l phosphate (ortho/poly 70/30) | with 2 mg/l phosphate (ortho/poly 70/30) + 2 mg/l silicate |

Figure 10: copper samples after cathodic polarisation

Looking at the photos it is quite obvious that the inhibitors applied here had a significant effect on the cathodic reaction because the surfaces of the respective samples do not show any visible precipitates. The calcite precipitates on the surface of the sample exposed to the non-inhibited water seem to be randomly distributed and therefore one can speak of a heterogeneous calcite layer with weak protecting characteristics. In contrary, it is likely that a homogenous thin (and therefore invisible) layer of calcium phosphate with protecting abilities has formed on the surfaces of the other samples. This correlates with the lower oxygen diffusion limiting currents of these samples as shown in Figure 6. The occurrence of calcium phosphate layers due to the application of phosphate-based corrosion inhibitors has also been reported by other researchers [1; 14].

4   Discussion and outlook

Previous work (unpublished) with the electrochemical methods applied here has revealed that an influence of the anion content of a given water on the pitting potential of a copper sample can be shown by anodic polarisation.

In the investigations described here the anodic differences appear not that significant by looking at the pitting potentials. This is not surprising as most inhibitors are influencing the surface layer characteristics and therefore the cathodic reaction.

This is supported by the significant differences in the oxygen diffusion limiting currents derived from the cathodic polarisation experiments.

This emphasises the necessity to combine the electrochemical investigation of both the anodic and the cathodic reaction. Together with the analysis of the surfaces and of the pits after polarisation it is possible to get sufficient information about the effects of the respective inhibitor.

The combination of these evaluation methods showed that the water tested here is able to support active pitting corrosion on copper samples. This can be seen by the pitting potential, the oxygen diffusion limiting current and the distribution and depth of pits after polarisation. In addition, it seems to form inhomogeneous calcite layers with less protective abilities.

The other samples which were exposed to the same water, but with addition of different inhibitors delivered different results. The values for both the pitting potentials and the oxygen diffusion limiting currents as well as the surface analyses indicate an efficient inhibition more or less significantly.

These findings show that the combination of methods presented here is a quite useful tool for rapid testing. Due to the relatively short test periods the results derived by the described methods are not to be seen as absolute values, but compared to each other they can show up tendencies in the effects of different corrosion inhibitors on the pitting corrosion of copper pipes in drinking water. The rapid testing method presented here can be used as a kind of screening for available corrosion inhibitors to be shortlisted for further detailed investigations in a given drinking water.

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