

**Influence of drinking water treatment processes on the pitting corrosion
behaviour of copper pipes in domestic installations**

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Abstract

Internal pitting corrosion of copper pipes in domestic copper installations is a rare but costly problem. It is well recognized that the chemistry of the drinking water passing through the pipes can influence the formation and propagation of pits. Until today, not all limiting conditions of water characteristics for the initiation, stabilisation and repassivation of pitting corrosion in domestic copper installations are known, especially the activation of repassivated pits in aged copper pipes when changing the water quality significantly. Reliable indicators to evaluate which change of water parameters leads to stabilization of pit growth are still lacking.

Methods to investigate the corrosion likelihood of pitting in the case of a significant water quality change are introduced. Also an outlook at the development of a new method for the evaluation of the influence of the water quality on pitting corrosion is presented.

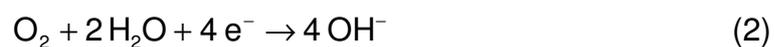
Introduction

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

The anodic reaction is the metal oxidation and follows equation (1)

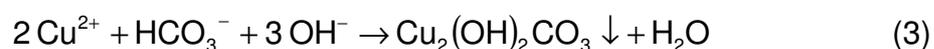


At the cathode the oxygen in the water is reduced (equation (2)):

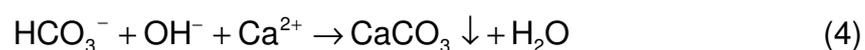


It has to be considered that also the water constituents take part in these reactions, for example calcium ions and hydrogen carbonate ions.

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



The resulting secondary reaction at the cathode is the formation of calcium carbonate (equation (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 the passivation of the system. Under unfavourable conditions also local processes, for example pitting corrosion, can take place [1].

The type of copper pitting corrosion can be determined by the morphology of the local attacks which is dependent on the water composition, the water temperature and the service conditions.

Type I occurs only in cold drinking water, while type II is limited to hot drinking water. A modified form of type I is type III, occurring in very soft drinking waters. Another type is the microbially influenced corrosion (MIC), where the attack is accelerated by microorganisms living in drinking water biofilms. To complete this list, the erosion corrosion has to be mentioned as another form of localised corrosion.

This paper will focus only on pitting corrosion type I.

Pitting corrosion Type I

There are several factors influencing internal pitting corrosion on copper pipes in drinking water installations

- § the material itself (manufacturing and processing),
- § the operating conditions of the installation
- § and the water composition [2].

The influence of material and processing mainly refers to the initiation process of pitting. Defects of the primary oxide layer on the inside wall of the pipe, inhomogeneities or the formation of copper(II) oxide layers by hard soldering cause the corrosion likelihood to local attacks. The surface characteristics also determine the pitting potential. The initial pitting potential is the lowest value of the corrosion potential at which pit initiation is possible on a passive surface in a given corrosive environment.

The operating conditions influence the pitting corrosion process in two different ways. In the initial phase, long stagnation periods of the water in the pipe and laminar flow conditions promote a stabilisation of local elements on the surface by the lack of transport of corrosion products. The phase of stabilisation and progress of the corrosion process is affected by the delivery of oxygen to the cathode. Here the typical flowing conditions during usual service are crucial.

The composition of the water plays a special role in the system of pitting corrosion as it influences both the anodic and the cathodic reaction, and additionally it interferes in the different phases of pit growth. Initiation and pit growth is determined by the interaction of the anions sulphate, nitrate, chloride and hydrogen carbonate. The influence is determined by the ratio of the anions rather than by the concentration of individual anions. However, a critical anion quotient cannot be indicated given the present state of knowledge. With respect to the typical influence of the anions (corrosion promotion or corrosion inhibition) the following (hypothetical) relationship for the anodic part of the pitting process can be connected (equation (5)).

$$LK = \frac{f_1 2c(\text{SO}_4^{2-}) + f_2 c(\text{NO}_3^-)}{f_3 c(\text{Cl}^-) + f_4 c(\text{HCO}_3^-)} \quad (5)$$

The relationship is in so far complicated as the anions have different corrosion em-phases, which is shown by the factors f_1 to f_4 in the equation. The emphasis of each of these factors is not known yet [3].

The main factors affecting the cathodic part of the pitting process are 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.

All the influences mentioned above indicate that pitting corrosion is a system of multiple factors and that it only occurs in the coincidence of critical factors.

Morphology of the inner surface of copper pipes

The usual formation of a surface layer on copper in hard to moderately hard waters happens by the development of micropits which are covered by malachite (Figure 1), until a closed layer exists. That means that the pits are closed with malachite caps and repassivated.

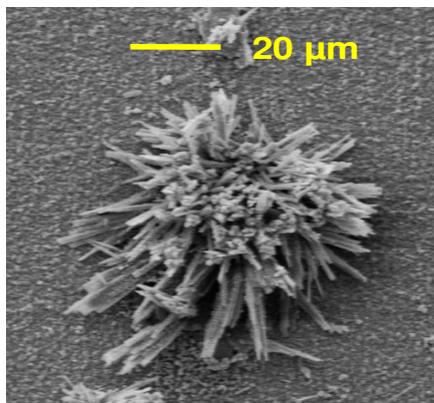


Figure 1
Microscopic picture of a malachite structure covering a micropit

Under unfavourable conditions anodic areas develop which cover with malachite tubercles (in softer waters with high sulphate contents with brochantite tubercles), form an isolated surface area and, according to the conditions, lead to active pitting corrosion. These areas are characterised by small channels or open tower-like structures with tunnel formation so that an exchange of material with the bottom of the pit is possible. Such a structure can be seen in Figure 2.



Figure 2
Microscopic picture of a tower-like malachite tubercle

It is especially dependent on the water composition which of the above mentioned states (repassivation or active pitting corrosion) will develop.

If the water composition in a supply area is to be changed significantly, it is necessary to consider the possible impact on the metallic materials which are already installed, meaning both: the water network and the drinking water installations of the

consumers. In the case of the latter, especially older installations where hard soldering was used as a joining technique were noticeable in terms of damage by pitting corrosion. But considering the fact that until 1996 almost all installations were connected by hard soldering in Germany, a huge number of installations is affected.

Influence of the water composition on pitting corrosion of copper

As already mentioned, the water composition has a major influence on pitting corrosion, mainly the anions chloride, sulphate and hydrogen carbonate with the following properties:

Contrary to the situation with other metallic materials, chloride acts as a passivating agent in natural waters in contact with copper. Sulphate and – to a certain extent – nitrate have an activating effect while hydrogen carbonate serves as a buffering agent. All of these anions influence each other in terms of their potency.

In the case of water treatment by chemical softening, for example, the content of hydrogen carbonate is decreased. That would declare this sort of water treatment basically as a pitting corrosion promoter because the content of the buffering agent is decreased. It is not known if there is a critical system-dependent concentration, which itself is dependent on other factors of the whole corrosion system. Another not well known point in this issue is the removal of so-called natural inhibitors (organic water constituents, for example amino acids) by membrane filtration processes.

It has to be found out if the application of corrosion inhibitors can compensate the decrease of the buffering agent, especially in the phase directly after changing the water composition. Here it is necessary to know, which minimum dosage of inhibitor is needed and what happens if this dosage is undershot or the inhibitor is not suitable for the corrosion system.

For a better understanding of the mechanism of pitting corrosion of copper and the influence of the water models have been developed. One of these is the membrane cell model by Lucey [4] which is shown in Figure 3.

Figure 4 shows photos of a copper pipe damaged by pitting corrosion where the morphology of the attack corresponds quite well with the Lucey model.

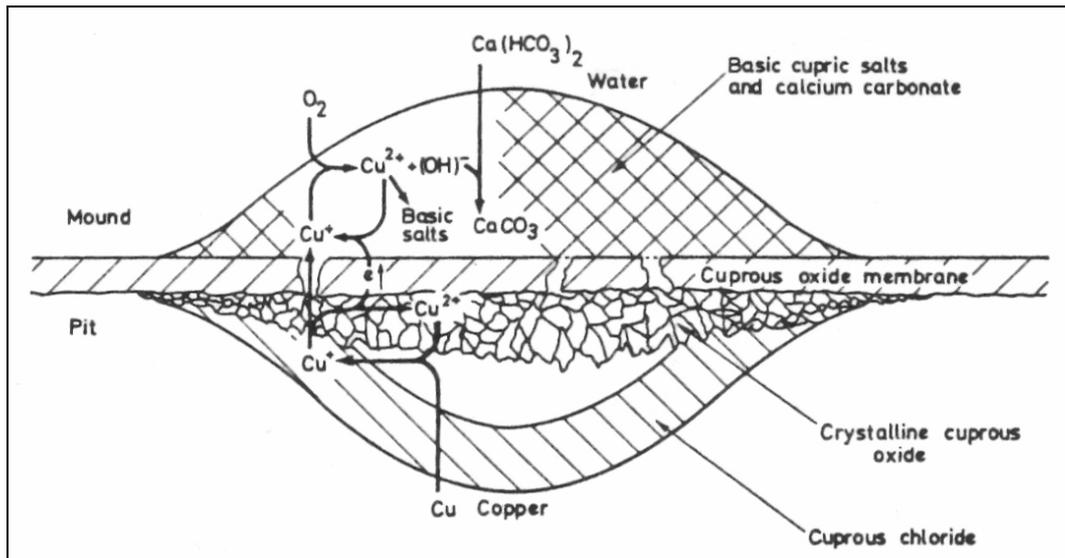


Figure 3 Membrane cell model by Lucey [4]

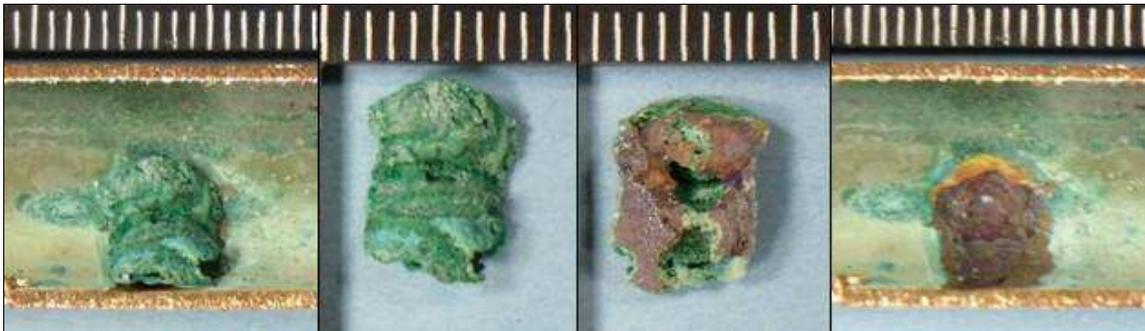


Figure 4 Photos of a copper pipe damaged by pitting corrosion

At the level of the original copper surface the whole area of attack is covered by a layer of Cu(I) oxide, which serves as a membrane. Below this there are variable amounts of coarsely granular Cu(I) oxide and fine Cu(I) chloride. There are small pores in the oxide layer at the level of the original copper surface, while the area below the green tubercle consisting of basic copper salts shows an extensive undermining attack.

On the inner side of the membrane Cu^+ is oxidised to Cu^{2+} (anodic reaction). These Cu^{2+} ions diffuse to the bottom of the pit and react to Cu^+ with the metallic copper. A part of these Cu^+ ions diffuses through the membrane and is oxidised by dissolved oxygen. The so-formed Cu^{2+} ions are either reduced back to Cu^+ at the cathode (outer side of the membrane) where they can also be oxidised again, or they can form basic copper(II) salts and calcium carbonate under participation of hydroxide ions from the oxygen reduction and calcium hydrogen carbonate [5].

Considering the model and the reactions involved the formation of Cu^+ and Cu^{2+} can be seen as chain reaction. This could result in a very high velocity of copper dissolution as the amount of Cu^+ formed is bigger. But the mass exchange is limited by the velocity of the electrons released to the oxide layer which is dependent on the delivery of oxygen from the water which takes up these electrons [3].

The activity of the anode can be reduced by removal of copper ions from the anodic area. This is achieved, for example, by the formation of hardly soluble compounds or by diffusion and migration into the electrical field outside of the pit.

In the case of a change of water composition a repassivated pit can be activated, for example, by the transfer of chloride and sulphate to the anodic area. This would result in an acidification of the bottom of the pit by acid hydrolysis which is easier the less the pit is buffered [5].

This model also has its weaknesses. The experiments which led to this model have been revised by Sosa and colleagues and they found out that more than 80% of the galvanic current flow away via the metal and not the bipolar membrane [6]. Despite these doubts about the model it serves quite well to explain the basic reactions and mechanisms involved in pitting corrosion of copper.

Test methods

For a better understanding of the processes of copper pitting corrosion and to be able to find answers to the open questions concerning a change of water quality a test program was developed and is continuously optimised. The base of these tests is a combination of surface analysis methods and electrochemistry.

Surface analysis

The tests and test rigs are designed in a way that they fit real life conditions as close as possible for a better correlation. On the other hand the conditions have to be sufficiently tightened so that pitting corrosion can occur under controlled conditions. In this way also a worst-case-scenario is created.

As mentioned before, hard copper pipes where hard soldering was used as the joining technique, are most vulnerable to pitting corrosion. Therefore the process of hard soldering was simulated by treating commercially available hard copper pipes with a burner similar to one which is used for hard soldering. The tip was pointed with a defined distance and for a defined time at a slowly rotating pipe to obtain equal heat distribution around the whole pipe diameter in the respective areas. In this way each pipe is prepared with four heat affected zones.

Figure 5 gives some insight into copper pipes prepared in this way.

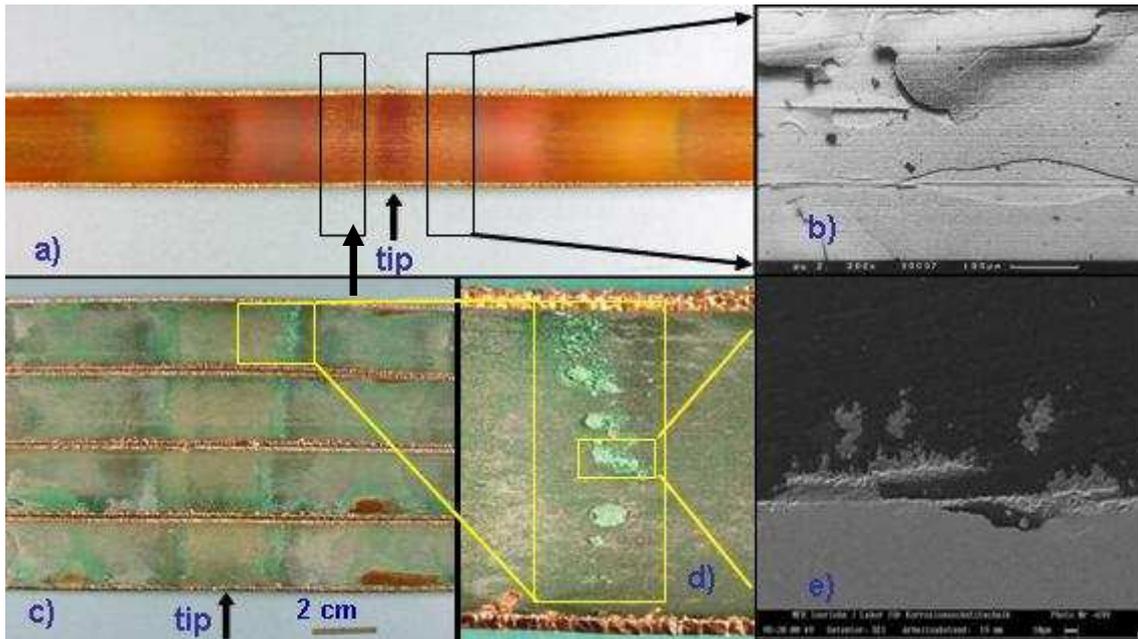


Figure 5 Copper pipes after preparation by simulated hard soldering

Picture a) Figure 5 of shows a horizontally sliced copper pipe after heat treatment. The black rectangles show the areas where pitting corrosion is most likely to occur. They begin approximately one to one and a half centimetres left and right from the point where the tip of the burner was, and reach out about one and a half centimetres further. A scanning electron micrograph of a heat treated area is shown in b), where the defects in the thermal oxide layer are clearly visible. The three pictures at the bottom of Figure 5 give an example what the inside surfaces of the heat treated pipes can look like after exposition to different waters. In picture c) one can see the areas around the tip where numerous corrosion tubercles have developed (yellow rectangle). A detailed sight of this area is given in d), while e) is a cross section of it showing the pit under the tubercle.

The exposition of the prepared pipes to the different waters of interest is done by placing them in a test rig with multiple strings so that different water compositions can be compared. The test rigs are operated with a defined program of flow and stagnation to simulate the usual flowing conditions of water from a domestic installation. An example of a test rig installed in a water treatment plant is given in Figure 6.



Figure 6
Test rig for the investigation of the copper surface and pit morphology

After certain time intervals (often several weeks) one pipe of each string is taken from the test rig for investigation. The pipes are sliced horizontally and the surfaces are documented by photography.

After removing the corrosion products by pickling the surfaces are investigated by the use of a microscope. The depths of the pits are measured by optical focussing. That means that one has to focus on the edge of the pit and then in a second step on the bottom. As the focussing is done by altering the height of the objective, the difference (in μm) between these two points equals the depth of the pit. It is measured by a fine instrument installed on the focussing unit of the microscope. In this way the distribution of pits and their growth can be investigated and evaluated statistically. The result of these measurements in combination with morphological investigations is a differentiation between pits representing

- § typical uniform corrosion (pit depth < $80 \mu\text{m}$)
- § active pitting
- § repassivated pitting.

Electrochemistry

As indicated in the introduction, corrosion reactions are of electrochemical nature. Charge carriers, meaning electrons and ions, are continuously passing through the phase boundary, resulting in measurable currents. Their extent is determined by the electrical resistance at the phase boundary. An established method is the recording of current density potential curves. A first step would be the determination of the free corrosion potential, without a current applied to the system. It characterises the driving force of the corrosion reaction under comparable conditions. The actual method of recording current density potential curves is based on the application of a direct current in an appropriate test arrangement which results in a measurable change in the potential. This method is called galvanodynamic polarisation. By plotting these values one gets the current density potential curves (Figure 7).

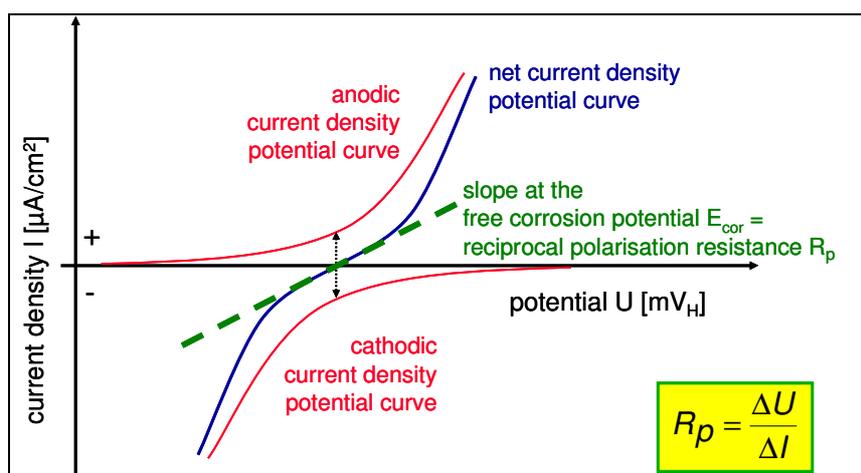


Figure 7
Current density
potential curves
(schematically)

Galvanodynamic polarisation shifts the potential either in anodic (positive) or in cathodic (negative) direction so that every potential value can be associated to a current value, resulting in a curve. The anodic corrosion processes accord to the anodic partial current density potential curves while the cathodic corrosion processes accord to the cathodic current density potential curves. These curves can be combined to a

net current density potential curve. At a certain point, the anodic and cathodic current, respectively, are equal so that no current is measurable. Therefore this point is called the free corrosion potential. Often the current density is plotted logarithmically (Tafel plot), which results in a reflection of the cathodic partial curve along the x-axis into the positive region. Thereby so-called Tafel-slopes can be determined which probably show linear areas [7].

The shift of the potential enables to derive the development of the driving force of the corrosion reaction from the associated current density. A high current density represents a high degree of material conversion, meaning a high corrosion velocity. Thus the inhibition of the activities of the respective partial reactions can be assumed from the steepness or flattening of the curves.

As indicated in Figure 7 the slope of the net current density potential curve at the free corrosion potential is a direct measurement for the sum of all resistances of the complete system. The reciprocal slope equals the polarisation resistance R_p which characterises the relative change of the complex resistance system. R_p is directly proportional to the corrosion resistance of a complete corrosion system.

Electrochemical tests in this work were done by the use of self-developed ring columns. They consist of a variable number of rings made of the material of interest (here: copper), separated from each other by plastic spacers. All these pieces are, including a holder for the reference electrode, pressed together with PE-flanges and thread rods (see Figure 8). This column can be installed in a test rig or even in a real installation (via a bypass). Water can flow through it like through a pipe and measurements can be conducted by an appropriate test arrangement.

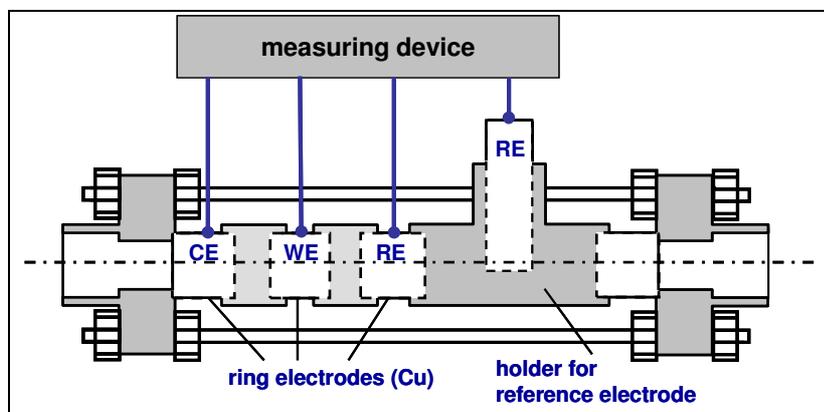


Figure 8
Ring column for electrochemical tests (schematic)

An example of a test rig installed in a water treatment plant with several different ring columns exposed to different waters is shown in Figure 9. It is the same water treatment plant and therefore the same waters and conditions as for the surface analysis test rigs mentioned above. Every single ring column is electrically shielded by a Faraday cage to avoid stray currents of the surroundings from disturbing the measurements.



Figure 9
Ring columns installed
in a test rig with and
without Faraday cage

The electrochemical test arrangement consists of the classical three-electrode-set-up. One copper ring serves as the working electrode where the current is applied. A silver/silver chloride electrode is installed in the holder for measuring the potential and a second copper ring serves as counter electrode to close the electrical circuit. In special cases the third ring electrode may be used as a reference electrode, too.

The electrodes are connected to a potentiostat. This device is the current source on the one hand and the measuring instrument on the other hand. It is connected to a notebook which collects the data and plots it with special software.

Results

In the following chapter some characteristic results of the test concepts explained above are presented.

Surface analysis

The heat treated copper pipes installed in the test rig were investigated according to surface appearance and pit morphology as well as pit growth. The aim was to show the influence of chemical softening of a hard groundwater with a relatively high neutral salt content on the pitting corrosion behaviour of copper. In Figure 10 the topographies of the respective copper surfaces and the distribution of the deepest pits for the water before and after softening are compared. The left hand part shows the results for the hard water, the right hand part for the softened water. In the lower graphics the maximum pit depth (in μm) is plotted against the service time of the respective pipe (in weeks).

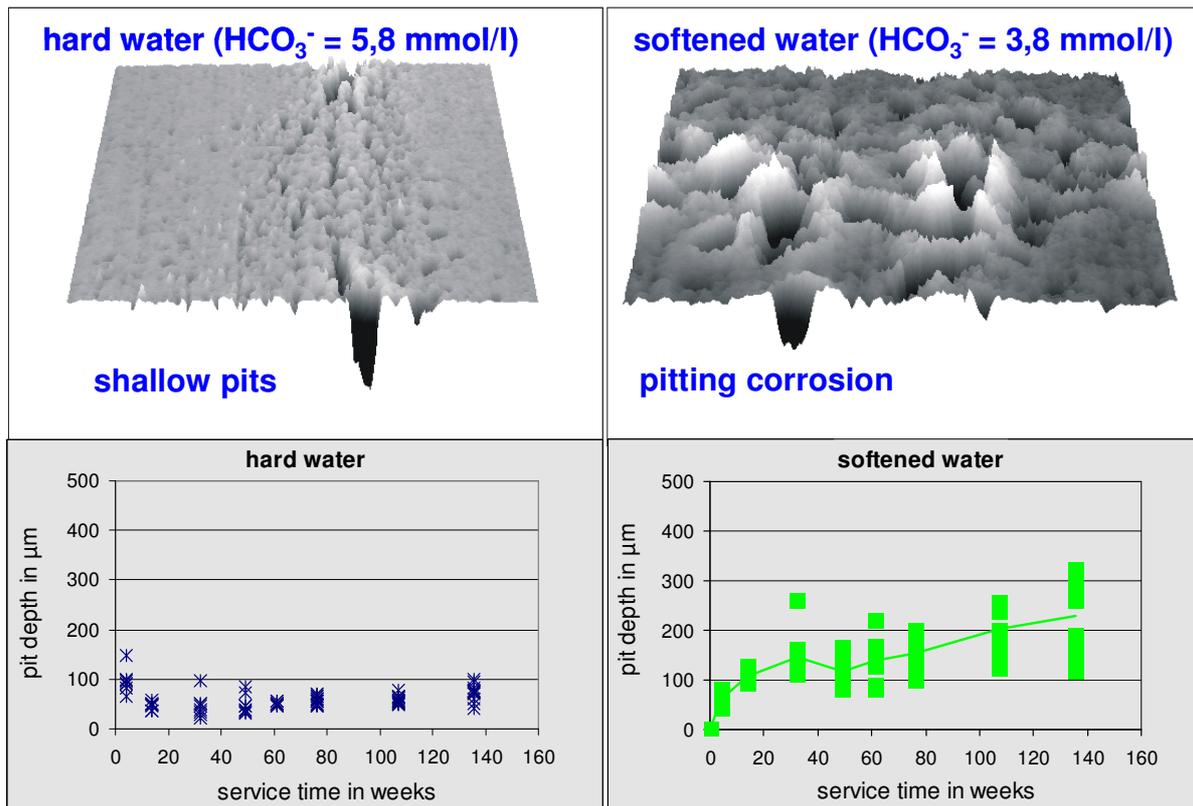


Figure 10 Comparison of surface topography and pit growth on copper in two different waters

Figure 10 clearly indicates that the softening of the water had a detrimental effect for the copper pipes as it activated pitting corrosion. While the hard water only caused shallow pits not increasing significantly in depth over time (indicating repassivation) the softened water showed active pitting corrosion with increasing pit depths over time. This results support the theory that the removal of the buffering agent hydrogen carbonate may promote pitting corrosion.

In the same project, also the effect of different corrosion inhibitors has been investigated. Two graphics, similar to those in Figure 10, were chosen to introduce the most interesting results. They are presented in Figure 11. The left hand part shows the influence of the dosage of a mixed phosphate inhibitor (ortho- and polyphosphate) to the softened water and the right hand part shows the influence of the dosage of a silicate inhibitor to the hard water.

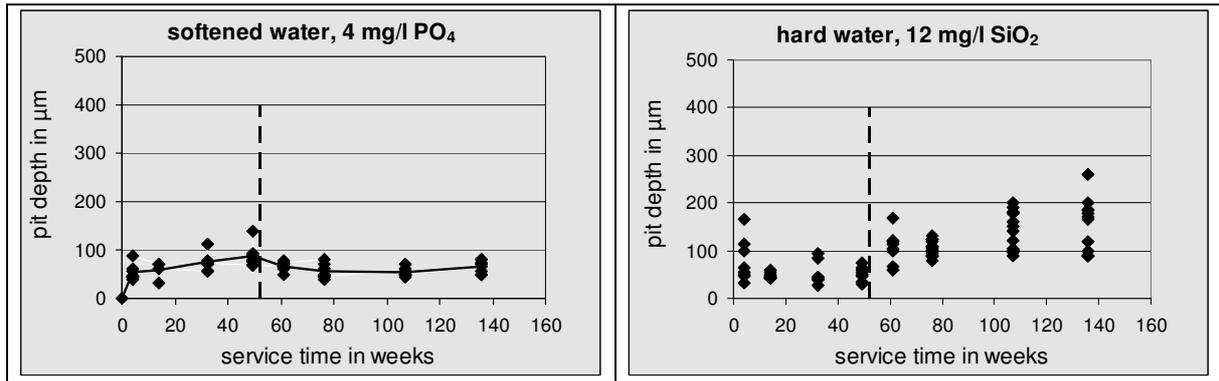


Figure 11 Results for the dosage of different inhibitors

The two graphics of Figure 11 show that the dosage of the different inhibitors to the different waters has somehow reversed the respective effects which were shown in Figure 10. The phosphate inhibitor in the softened water led to repassivation of the active pitting corrosion which occurred without it. On the other hand the silicate inhibitor seems to have activated the repassivated shallow pits which occurred in the hard water before.

These results indicate that it is important to know if the inhibitor which is planned to be applied can really inhibit pitting corrosion or if it even can worsen the problems like the silicate inhibitor in this case. Therefore tests like those presented here should be carried out in advance.

Electrochemistry

The following graphics present some selected results of the galvanodynamic scans. In each of them the current was plotted logarithmically against the potential. The cathodic partial curves were plotted in negative direction (left) from the free corrosion potential while the anodic partial curves were plotted in positive direction (right) from the free corrosion potential.

In Figure 12 the scans for three different surface conditions of copper in the same water are compared. The conditions are hard, half-hard and hard with heat treatment (simulation of hard soldering). Below that the corresponding scanning electron micrographs are shown.

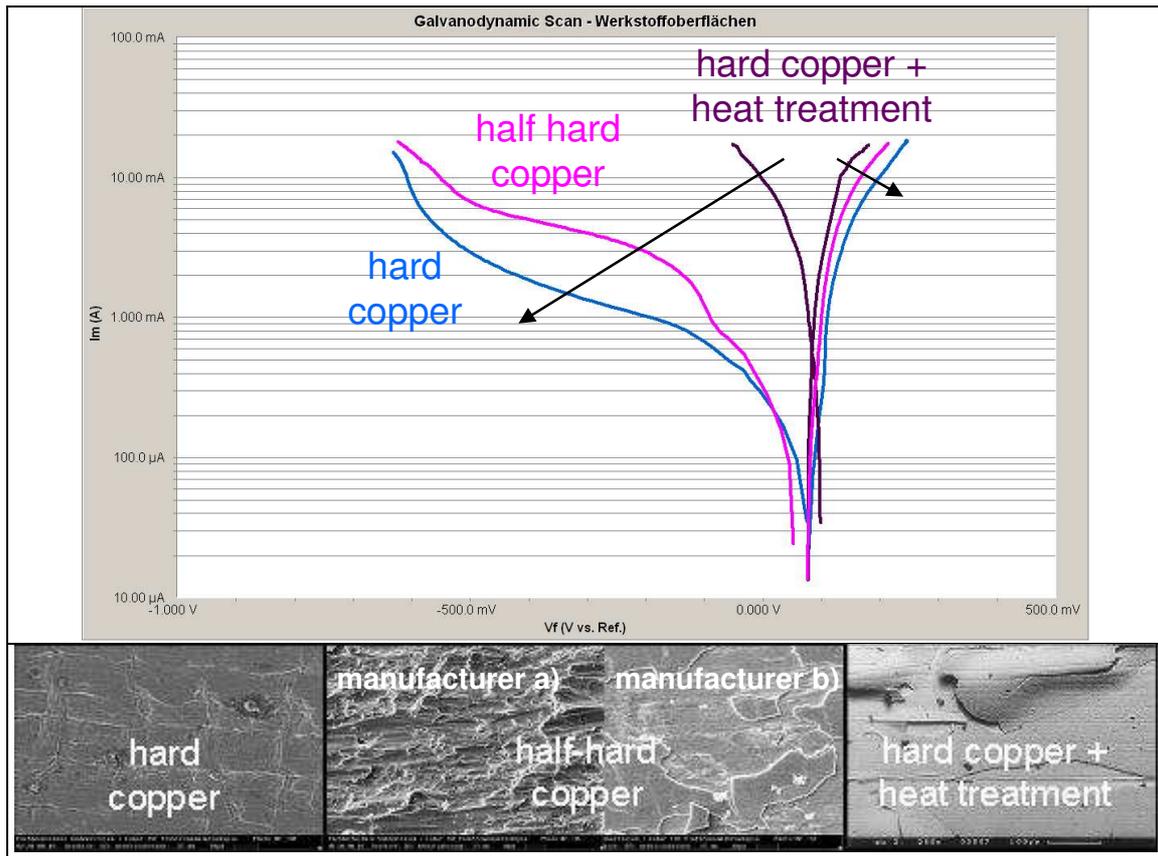


Figure 12 Galvanodynamic scans of three different surface conditions of copper in the same water and the corresponding SEMs

It can be recognised that the different surface conditions can be elucidated quite well using the technique of galvanodynamic polarisation. This electrochemical technique is based on slightly disturbing the corrosion system at the phase boundary between material and corrosion medium using small amounts of direct current. The magnitude of the resulting potential shift depends among others on the consistency of the inner surface of the copper tubes directly at the phase boundary.

The more significant effect can be seen at the cathodic partial reaction, while the differences at the anode are only marginal. This indicates that the inhibition of the corrosion process in the initial phase is mainly a result of the properties of the copper oxide layer serving as cathode.

The graphic underlines that the heat treatment of the hard copper pipe leads to the most active surface compared to the two other ones. This is due to the defects in the copper(II)-oxide layer caused by the heat treatment. This can be seen on the SEM as well as in the steepness of the curve.

In contrast to that the hard copper pipe without heat treatment shows a relatively homogenous surface and therefore the slope of the cathodic curve of the galvanodynamic scan is much flatter. That means that this surface is less active than it is after heat treatment.

The curve of the half hard copper pipe is lying between the other two mentioned before. Its surface is covered with an inhomogeneous layer of copper oxide due to its

production process. This can be seen on the SEMs in the lower middle of Figure 12 as well as in the slope of the respective cathodic curve.

These results corroborate that the likelihood of pitting corrosion can partially be related to the surface condition of the copper pipe and that this can be investigated by electrochemical methods.

Figure 13 presents some results of laboratory-scale electrochemical tests. In these experiments a piece of a hard copper pipe was immersed in the water of interest. Potentiodynamic scans were performed here which means that the potential of the copper was changed with a very slow scan rate while the corresponding currents were measured. The graphical presentation of the results is the same as for the galvanodynamic scans.

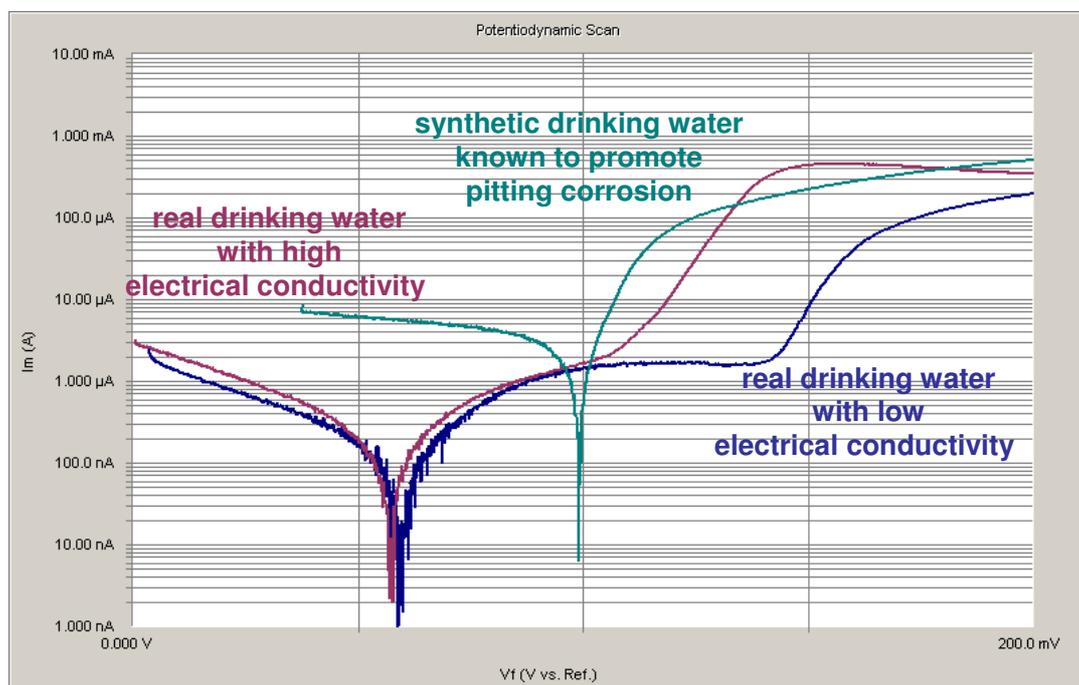


Figure 13 Results of potentiodynamic scans of hard copper pipes in different waters

Aim of these investigations was the determination of the pitting potential as the critical potential, where pitting corrosion begins to occur [8]. Therefore the anodic polarization was of the preferring interest.

The anodic parts of the curves of the two real drinking waters show a significant passive area, meaning the area where the current is not increasing. When the current starts to increase again, the systems pass into the active state. At this transition between passive and active the pitting potential can be estimated. In this case the lower electrical conductivity of one of the waters caused a shift of the pitting potential towards more positive values which indicates that this water is less pitting promoting towards hard copper pipes.

The curve of the synthetic drinking water which was known to promote pitting corrosion showed a completely different behaviour. The free corrosion potential was

shifted significantly towards more positive values and the system passed directly into the active state. That indicates that the pitting potential is very close to the free corrosion potential and thus it is reached much easier and faster.

The results of the potentiodynamic scans show that this technique has the potential to aid in comparing the influence of different waters on the pitting corrosion behaviour of copper pipes.

Conclusions and outlook

Considering the information given in the introduction the conclusion can be drawn that copper pitting corrosion is a problem with multiple factors. One major factor is the composition of the water. Hence the roles of the other factors (material and operating conditions) are elucidated to a large extent, the role of the water and its constituents can only be estimated yet. This especially holds for the role of the mentioned anions and their interaction.

Combining these facts with the results presented here leads to the conclusion that a significant change of the water composition, for example by changing the treatment technique or by applying an inhibitor, can lead to the activation of pitting corrosion under unfavourable conditions. This especially holds for older drinking water installations made of hard copper pipes with hard soldering as the joining technique.

That means that prior to these measures in critical supply areas a corrosion chemical evaluation should be carried out. If this is revealing an unfavourable situation, practical tests like those described above are recommended to avoid the occurrence of possible problems with pitting corrosion.

The results have shown that the combination of electrochemistry with surface analysis like the characterisation of pit growth is a suitable tool for an estimation of the risk potential.

Here a uniform and manageable testing and evaluation procedure would be helpful, which is currently under way.

This research is done in the context of a doctoral thesis dealing with the influence of different drinking water treatment techniques on the activation and repassivation of pitting corrosion in copper pipes in domestic drinking water installations. That work is carried out by applying the methods explained above, among others, and their continuous improvement and optimisation.

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