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Pitting corrosion of copper – current damages in drinking water systems in Germany

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Summary

Until 2003, in Germany damages only occurred in drinking-water installations with hard copper tubes (R 290, EN 1057) which were connected by hard-soldering (general joining technique until 1996 in Germany) or which were heated to bend (without the use of fittings). The significant heating may be crucial for the life prediction of the copper tubes generating pre-existing defects associated with changing the material structure and a sensitisation of the ground material. So, damages outside of the heating zones are not usual and are often associated with the initial start-up of the drinking water installation.
Current damages in Germany (since 2005) occur on copper tubes of the temper “half-hard” (R 250, EN 1057) within the copper tube and not associated to the fittings. Damages are known in cold and hot water. The reasons for these damages are not clarified. Damaged tubes show a noticeable amount of pits. There is no relationship to the connection technology (fittings) or geometry. Pits occur elsewhere also in pipes in vertical position. Currently there is no information of the influences of a special critical water composition.

1 Introduction

Among experts there is a general consensus that copper pitting corrosion is a system property where the parameters material, storage, processing, start-up, service conditions and water composition play a role. But only a coincidence of several unfavourable conditions determines the damage likelihood and its dimension.
For the damage development different stages of pit growth are crucial, which can be assigned to the parameters mentioned above. The processes of pit growth can be divided into the main processes of initiation (pit preformation), activation (unstable pit growth, active-passive element) and stabilisation (active pit growth). The main influencing factors here are the parameters material (including condition of material surface), water composition and operating conditions [1].
Until the middle of the 1990´s the damage symptoms were mainly determined by pitting corrosion in installations where copper pipes of the temper “hard” (R 290, EN 1057) had been hard-soldered or annealed (e.g. for bending). The partially significant pre-damage of the pipes due to the extreme heat treatment was determined as the primary cause of damage [3]. Since approximately 2005 increased numbers of damages have been noticed from installations where copper pipes of the temper “half-hard” (R 250, EN 1057) were processed. Some of these damages occurred in supply areas which had been considered as unremarkable for copper pitting corrosion. These damages affect both cold water and hot water systems. The causes of these pitting corrosion damages cannot be explained yet.

2 Forms of appearance of copper pitting corrosion

There are different types of pitting corrosion of copper in drinking water installations which can be differentiated by the morphology of the pitting attacks [2]. The type and the form of appearance depend on the water composition, the water temperature and the operating conditions. Copper pitting corrosion can therefore be classified into type 1 (cold water), type 2 (hot water), type 3 (modified form of type 1, restricted to very soft waters) and microbially influenced corrosion (MIC). Typical appearances of the types 1 and 2 are shown in Figure 1.

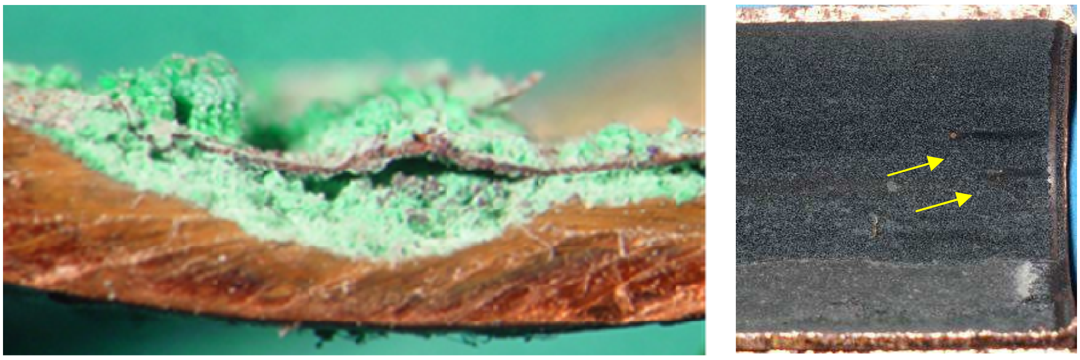

Figure 1: Typical appearances of copper pitting corrosion type 1 (left) and type 2 (right; damage sites marked with arrows)

3 Pitting corrosion damages in drinking water installations and influence of water composition

In the last three decades pitting corrosion of copper occurred – in the vast majority of the documented cases of damage – in cold water installations where hard-soldering was used as joining technique and/or where the pipes had been annealed for bending. Since these techniques have been banned from the technical rules in 1996, the damage likelihood for new installations decreased significantly. Due to the relevance and the large number of damages in single supply areas a series of research projects had been conducted in the past decades so that the causes and mechanisms of this form of corrosion can be explained – not yet completely, but to a large extent [1].
In the damage mechanism the process of hard-soldering plays a crucial role. The significant heat treatment can lead to a pre-damage of the pipe due to a structural change and a sensitisation of the parent material. Figure 2 shows the different appearance of the copper structure, dependent on the heat treatment.

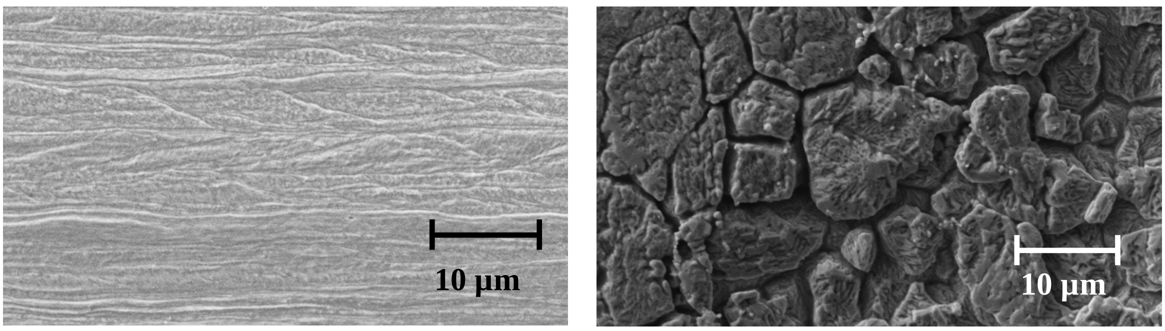

Figure 2: Different appearance of copper structure due to heat treatment (samples pickled in 10% citric acid; left without, right with heat treatment) [4]

The left picture shows the copper surface without heat influence, the right one shows the surface in the centre of the heat treatment zone. The local attack on the metal in these areas of structural change (after a heat treatment comparable to hard-soldering) occurs mostly along the grain boundaries and spreads over one to two grain layers. Therefore the heat treatment also leads to a sensitisation of the parent material which favours local corrosion processes. This can be seen in a cross-sectional metallographic specimen where the initial local attack spreads along the grain boundaries (Figure 3, left). In the further development of an active pitting site it appears as a spherical shaped shallow pit (Figure 3, right; pitting corrosion type 1).

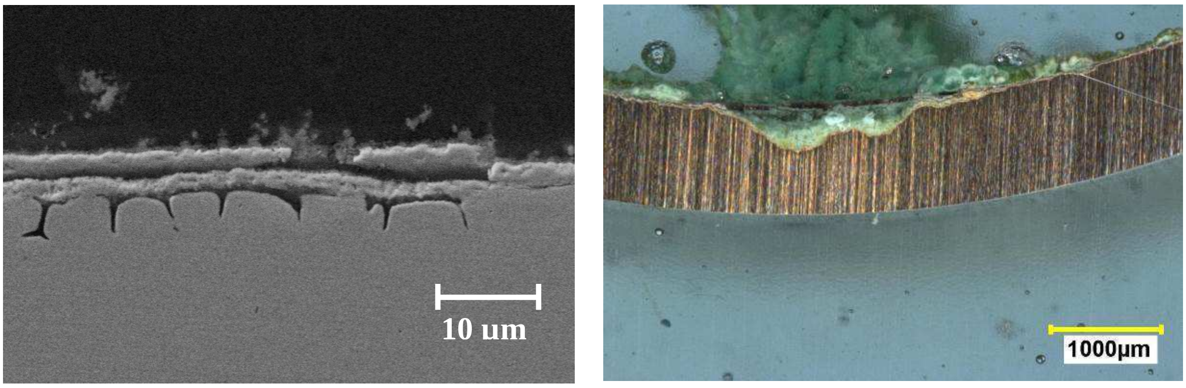

Figure 3: Cross-sectional metallographic specimen; left: example of a corrosion attack spreading along the grain boundaries of a heat treated pipe; right: spherical shaped shallow pit

Damages outside of the heat affected areas are unlikely in copper pipes of the temper "hard" and therefore require individual investigations. Normally these damages are coupled with problems of craftsmanship and/or start-up. Therefore the damage likelihood – with regard to the pre-damage of the pipes – can be primarily and relatively safely deducted to the processing.

This is different for pitting corrosion type 2 in hot drinking water. This type of corrosion played a minor role in Germany, but also in other European countries, in the past three to four decades. Problems mainly occurred in Scandinavia (especially in Sweden [5; 6]). Therefore research was done only sporadically on this topic so that the causes and mechanisms of this type of corrosion are extensively unknown.

Since 2003 damages are reported from supply areas where waters are distributed which differ significantly from those described in EN 12502-2 as being promoting for pitting corrosion type 2. EN 12502-2 contains the up-to-date state of international knowledge for the estimation of the corrosion likelihood of copper and copper materials in water distribution systems [7]. The water composition and the water temperature are considered to be the main influencing factors. The likelihood for pitting corrosion increases in waters which have a low pH (< 7), a low hydrogen carbonate (< 1.5 mmol/l) and a high sulphate content. The corrosion likelihood is high when the ratio between the molar concentrations of hydrogen carbonate and sulphate is smaller than 1.5. The critical water temperature is above 60 °C.

According to the compositions and the properties of the respective waters where pitting corrosion type 2 has been reported yet (acidic, soft waters, often self-supply where not all limiting values of the drinking water directive are met), the water-related countermeasures are recommended as follows: deacidification (raising of pH) and hardening (increasing the content of hydrogen carbonate) of the water [2].

Table 1 exemplary shows a comparison of the water parameters considered as pitting promoting as yet and the values of these parameters in the two water supply areas A and B, where pitting corrosion has also occurred.

Table 1: Evaluation of pitting promoting tendencies of the drinking waters A and B

parameter	pitting promoting conditions	supply area A	supply area B
pH	< 7,0	7,8 – 8,0	7,95 – 8,0
HCO_3^- [mmol/l]	< 1,5	2,2 – 2,5	2,9 – 3,0
SO_4^{2-} [mmol/l]	---	1,0	1,0
$S = \frac{c(HCO_3^-)}{c(SO_4^{2-})}$	< 1,5	2,2	2,9
T	> 60 °C	60 °C	60 °C

Except for the influencing factor "water temperature" both drinking waters shown here do not belong to the group of waters which can be described as pitting promoting, based on the up-to-date state of knowledge. The pH values are significantly higher than 7, and both waters are supplied as slightly calcite precipitating. The quotient S (ratio between hydrogen carbonate and sulphate) as a measure for increasing corrosion likelihood is also significantly higher than the anion ratio considered as critical. The countermeasures mentioned in the norm, namely the increase of pH, are not constructive for the waters A and B as they are already supplied as calcite precipitating.

The conclusion here is that the remarks in the norm EN 12502-2 do not comply with the cases of pitting corrosion damage in practice and that an evaluation of the damage likelihood in hot drinking water based on this norm is not possible.

This estimation also applies for the evaluation of the water-related influencing factors for damages by pitting corrosion type 1 (cold drinking water). Until today there are no authoritatively applicable evaluation standards for the application of copper pipes considering the corrosion resistance of the material in contact with drinking water.

The water-related specifications in the norm DIN 50930-6 exclusively apply for the hygienic evaluation of the drinking water quality with regard to copper release into the drinking water [8]. So the evaluation standard here is the corrosion-caused impairment of the drinking water quality with the possible danger of a no-compliance with the limiting value for copper, based on the drinking water directive.

The pieces of information provided in EN 12502-2 regarding the water-related influencing factors are not helpful because based on this norm an evaluation of single water parameters can only be conducted in a qualitative way. There are only qualitative statements towards the influence of single water parameters, namely hydrogen carbonate, chloride, sulphate and nitrate. The difficulty here is that not the absolute concentrations of these anions are considered to be decisive for the likelihood of pitting corrosion, but their ratio towards each other. Another complicating point is that the individual potency is different for each of these parameters, which also has to be considered when trying to assess or estimate the pitting promoting or the pitting inhibiting properties. When formulating a quotient which would relate the pitting inhibiting parameters (chloride, hydrogen carbonate) to the pitting promoting parameters (sulphate, nitrate), the single parameters would have to be multiplied with different constants which characterise their different potencies or rather their different degrees of influence on the corrosion process.

4 Current novel damages in drinking water installations made of copper

The current damage phenomena in copper installations can be characterised by the following statements:

- Damages in old, hard-soldered installations made before 1996 where damages occur either sporadically (wave-like development of damage maxima) or suddenly after long operating periods of more than 20 years.
- Damages of copper pipes of the temper “half-hard” in cold water as well as in hot water installations.

While in the former case the water composition might play a crucial role, the causes for today´s damages of half-hard copper pipes are completely unknown.
Some specific features are noticed in the novel cases of damage:

- damages are distributed around the complete cross-section of the pipe
- horizontal and vertical pipes are affected
- a partially high number of deep pits
- a partially high number of wall perforations relating to the pipe length
- occurring of a “half-shell-effect”, also in vertically installed pipes, which cannot be related to problems during the start-up (e.g. partial filling of the pipe)
- a noticeable morphology of the pits
- damages occur in single and multi-family houses as well as in larger installations like hospitals, retirement homes and schools

As described above, one of the specific features is the high number of pits (including perforation) relating to the pipe length. For clarification Figure 4 shows a comparison of perforations detected on the outside of hard-soldered copper pipes of the temper “hard” with normally one or two damages occurring simultaneously (upper pictures) and perforations detected on the outside of a copper pipe of the temper “half-hard” (picture below).

Figure 4: Comparison of the number of perforations of the pipe wall

In the case of the pipe shown in the bottom picture seven perforations were detected on a pipe length of 30 cm.
Damages are determined in cold and hot water systems and also occur extensively in water supply areas which have not been reported as noticeable corrosion areas yet. Damages are detected only in pipes, not in fittings yet.
In first orientating investigations some specific features have been found in the morphology of the pitting sites. The optical appearance of the covering of the pit and the

composition of the corrosion products equal the normal findings in cases of pitting corrosion type 1. That fact which has not been described for drinking water so far is the structure of the pitting sites. They show fine ramifications under initial corrosion conditions leading to tunnel-like branching which can spread into significant undercutting attacks (Figure 5).

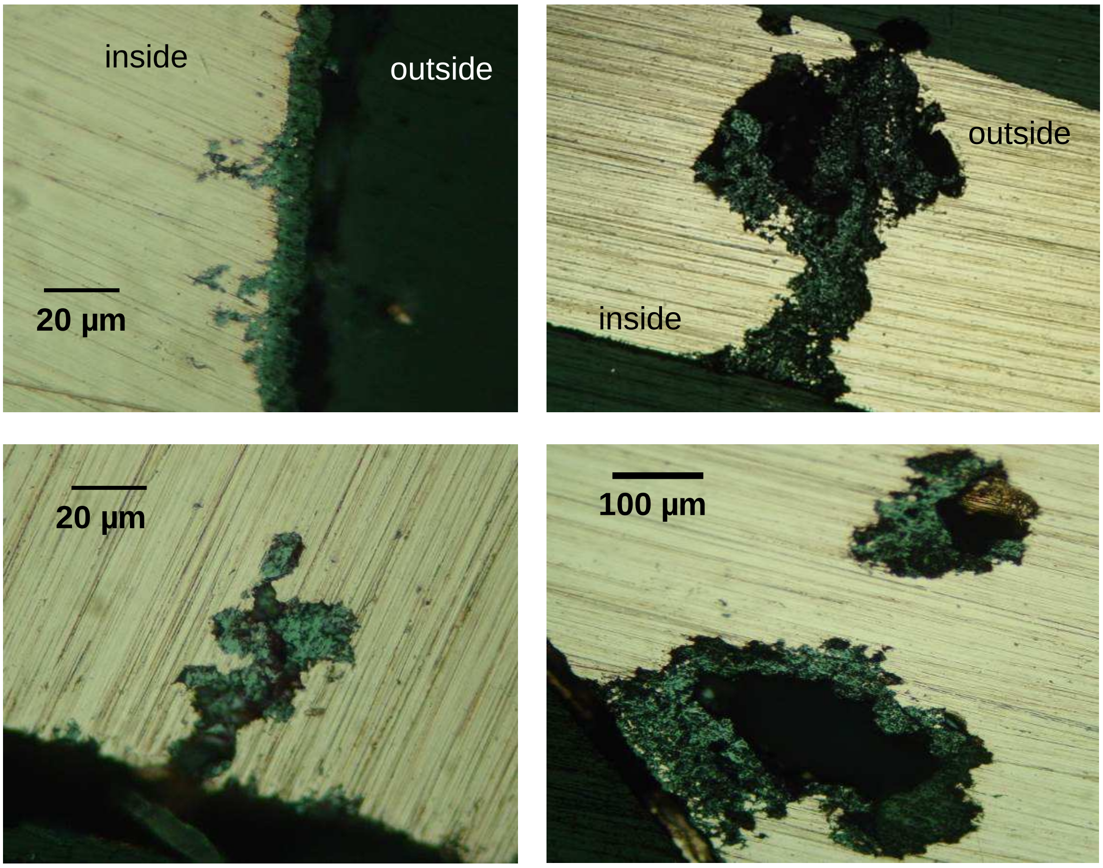

Figure 5: Structure of local corrosion attacks in copper pipes of the temper "half-hard"

There are no models available yet to explain the causes of these novel types of damage, which would be very necessary for an assessment of the danger of corrosion damage. Countermeasures are also not known so that often the only remedy for the affected user (e.g. owner of the house) – depending on the degree of damage and the damage prognosis – is to replace the complete copper installation. The application of corrosion inhibitors can be constructive, but there an individual solution has to be found, combined with testing and choosing a product compatible to the actual water composition.

5 Conclusions

In the past decades intensive research has been conducted regarding the causes of the "classical" pitting corrosion type 1 in cold drinking water. The results of this research have led to the exclusion of hard-soldering from the technical rules and the introduction of press-fit fittings, for example, which caused a significant decrease of the damage likelihood for copper pipes of the temper "hard". Nevertheless partially significant damages in cold and hot water systems are currently occurring in copper pipes of the temper "half-hard" which cannot be explained by the up-to-date state of knowledge. For an understanding of the underlying corrosion processes and especially for the clarification of the causes of these damages research is in great demand again [9].

6 References

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