The efficiency of corrosion inhibitors in the light of copper corrosion – results from field test studies

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1 Summary

Corrosion inhibitors are used in the drinking water sector since years in order to handle water quality problems caused by corrosion processes of unprotected iron pipes. Moreover, in the last years it was recognised that corrosion inhibitors also may be used in order to minimise copper release from copper pipes used in household installations. At the moment especially in Germany more and more water works are focusing on this possibility, in order to handle the limit value for copper, which is valid at the consumer's tap. For the evaluation of the efficiency of corrosion inhibitors regarding minimisation of copper release test rig experiments were carried out in more than 20 water works throughout Germany. With this paper selected results are presented.

2 Introduction

With the Council Directive 89/83/EC [1] the copper concentration in drinking water became more relevant. With the adoption of the European Directive in Germany for copper a limit value of 2 mg/L is given. Moreover, in the German Drinking Water Ordinance [2] with § 17 requirements for compounds and materials, which are used in the drinking water production and delivery, are given. It is pointed out that these materials have to comply with the acknowledged rules of technology. For copper pipes this means besides of the technical requirements DIN 50930-6 [3] "Corrosion of metals – corrosion of metallic materials under corrosion load by water inside of tubes, tanks and apparatus – part 6: Influence of the composition of drinking water" has to be regarded. With this technical standard operative ranges for the use of copper in drinking water installations in dependence of the water quality are given as follows: Copper can be used without having negative effects on the water quality if pH>7.4. If pH is between 7.0 and 7.4 the content of total organic carbon (TOC) must be below 1.5 mg/L. If the respective water quality complies not with these operative limits copper can not be used but one has the possibility to carry out tests according to DIN 50931-1 [4] "Corrosion of metals – Corrosions tests with drinking water – Part 1: Testing of change of the composition of drinking water".

In Germany many waterworks are using corrosion inhibitors in order to minimise water quality problems caused by corrosion processes in the water network. Therefore, different inhibitor systems are on the market, which contain ortho-/poly-phosphate and silicate or mixtures of these compounds. With the list of authorized water treatment agents and disinfection measures according to § 11 of the German Drinking Water Directive [5] the added amount concerning corrosion inhibitors is restricted with total 2.2 mg/L P and 15 mg/L SiO_2.

As already presented in the literature corrosion inhibitors can minimise copper release in individual cases [6]. Under the guidance of TZW meanwhile more than 20 field test studies at different waterworks throughout Germany were carried out which clearly demonstrate, that corrosion inhibitors affect not only iron but also copper corrosion.

3 Test method

For the field test experiments automated test rigs according to DIN 50931-1 were installed on-site and were operated between 26 and 104 weeks and each test rig comprised for each water quality in general two or three copper pipes with the mechanical property “hard”. The methodology given by DIN 50931-1 as well as the design of the test rig are already described in detail in the literature [7]. Here again one has to emphasize that in Germany mean values according to DIN 50931-1 are regarded as the sample being representative of a weekly average value ingested by the consumer.

4 Field test studies according to DIN 50931-1

4.1 Copper release

<u>Water work 1</u>

The water distributed by water work 1 has a total hardness of about 18 to 22 °dH. Oxygen content varies about 10 mg/L. The pH value is about 7.3 and the content of total organic carbon varies about 2 mg/L. Therefore, according to DIN 50930-6 copper can not be used for drinking water installations without any further testing. In order to investigate, whether or not corrosion inhibitors can reduce the copper release from copper pipes into drinking water ortho-phosphate containing inhibitors as well as phosphate/silicate inhibitor systems were tested. Results are shown in figure 1, where mean values according to DIN 50931-1 are presented.

As can be seen from figure 1 DIN 50930-6 is confirmed in this case because mean values according to DIN 50931-1 are throughout the whole test period of 2 years above the limit value of 2 mg/L Cu. But if corrosion inhibitors are dosed in the composition and concentration lined out in figure 1 the limit value for copper of 2 mg/L can be met. Moreover, one can conclude, that in this case 0,5 mg/L ortho-phosphate are sufficient to reduce copper release from copper pipes efficiently. Additionally, the results here demonstrate, that no significant difference is given whether 3 mg/L ortho-phosphate or a mixture of ortho-/poly-phosphate/silicate in concentrations of 0.7/0.3/6.0 mg/L are used. But it can be seen, that especially the efficiency of ortho-phosphate is depending on the used concentration. Reducing ortho-phosphate concentration leads to higher copper release. In this case, if phosphate dosage is stopped it takes about 20 weeks until copper release is in the same order as for the water, in which no corrosion inhibitors was dosed. Therefore, in this case phosphate has for a certain time period a repository effect.

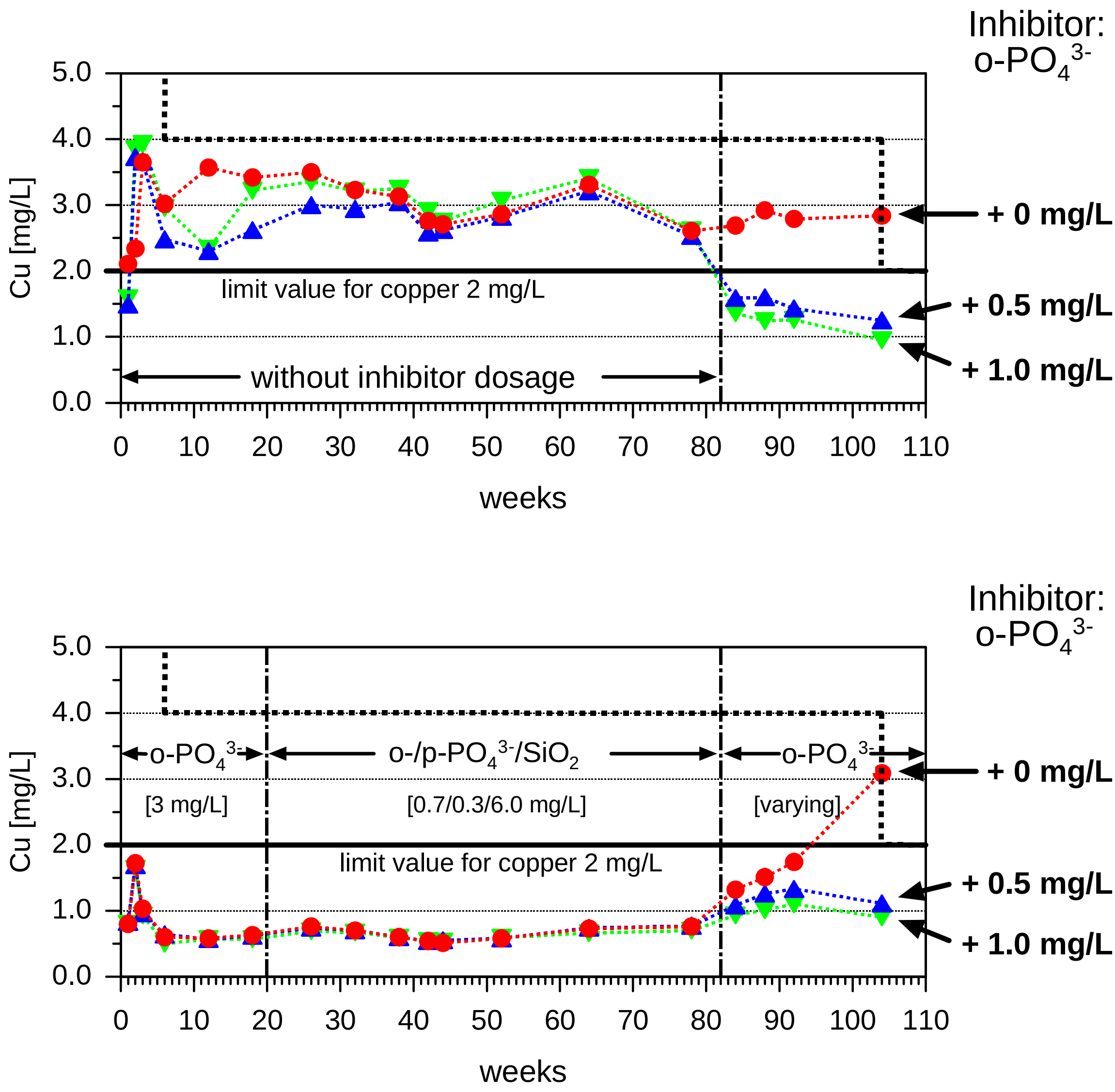

Figure 1: Mean values according to DIN 50931-1 in dependence of the running time determined within field test studies in water work 1

Having a more detailed view on the influence of ortho-phosphate on copper corrosion one has to look on the stagnation curves. These give for a certain running time the copper concentration in dependence of the stagnation time. In figure 2 the stagnation curves after 26 weeks for a copper pipe charged with drinking water from water work 1 (with and without ortho-phosphate) is presented. As can be seen ortho-phosphate influences dramatically the kinetic of copper release.

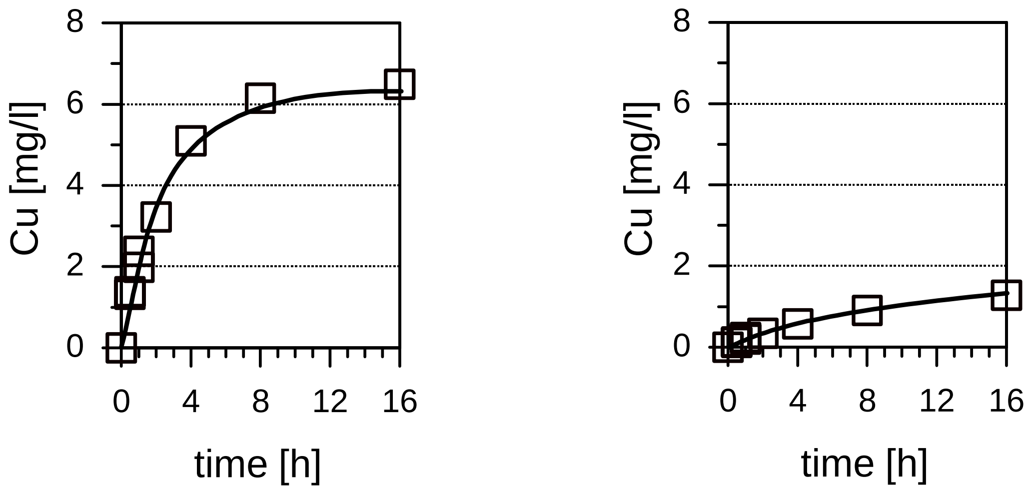

Figure 2: Stagnation curve for copper pipes charged with drinking water (left-hand side) and with drinking water containing 3 mg/L ortho-phosphate (right-hand side) after a running time of 26 weeks (water work 1)

<u>Water work 2</u>

The produced water of water work 2 has a hardness of 19 °dH. pH is about 7.3 and total organic carbon varies about 2 mg/L. Oxygen content is between 7 and 8 mg/L. Therefore, again copper can not be used according to DIN 50930-6.

In this case experiments according to DIN 50931-1 do confirm the operative limits given by DIN 50930-6, because mean values according to DIN 50931-1 are remaining after a test period of almost 2 years still above 2 mg/L Cu. In figure 3 results for two test pipes are presented. One test pipe was charged with the produced drinking water and after 82 weeks an inhibitor system containing o-/p-phosphate/silicate was dosed. Shortly after the dosage began copper release decreased significantly. Another test pipe was since the beginning of the field test charged with water containing different ortho-phosphate concentrations and after 63 weeks the inhibitor dosage was stopped. Again comparable to the results presented with figure 2 the efficiency of ortho-phosphate regarding minimisation of copper release is depending on the concentration. Moreover, it can be seen that after the dosage stopped copper concentrations increased immediately and consequently copper mean values were again above 2 mg/L.

Comparing this result with the results for water work 1 one can observe in principle similar effects but in contrast for water work 2 no respiratory effect of ortho-phosphate could be identified. Nevertheless, comparing the copper stagnation curves after 26 weeks running time, which are given in figure 2 and 4, the relative efficiency of ortho-phosphate in respect to copper release minimisation is nearly comparable in both cases presented here.

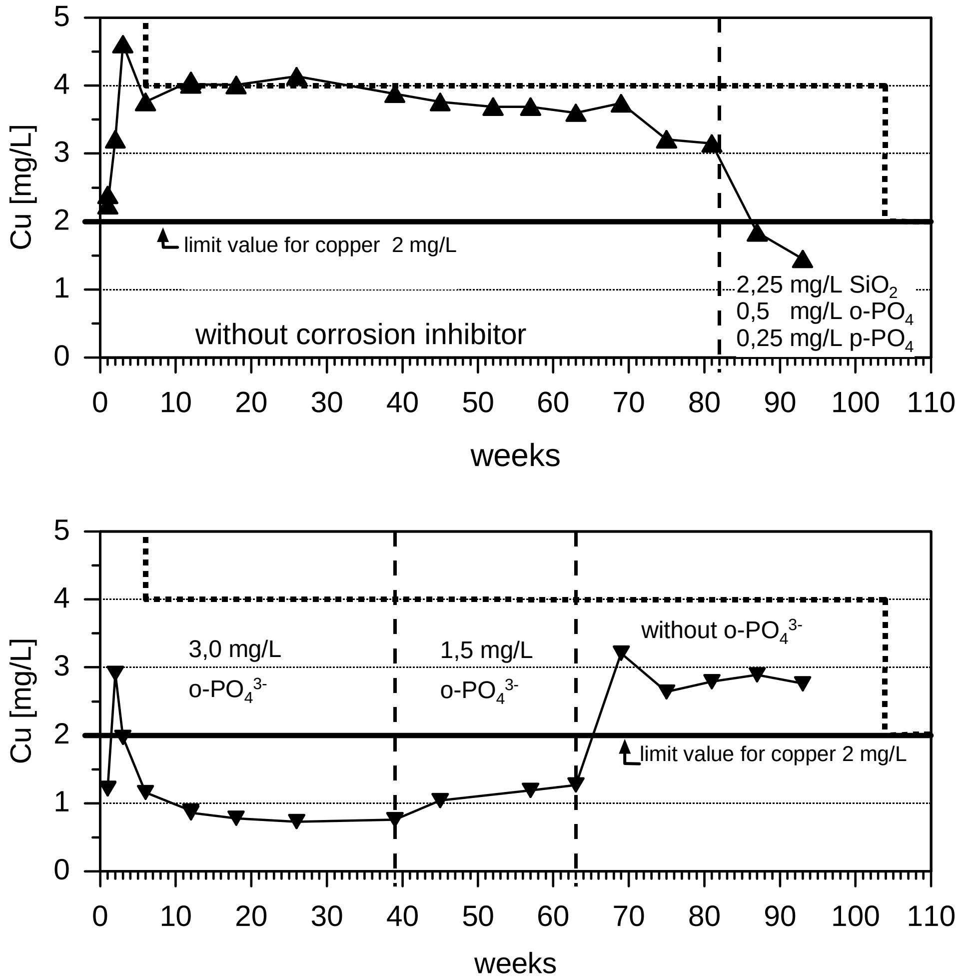

Figure 3: Mean values according to DIN 50931-1 in dependence of the running time determined within field test studies in water work 2

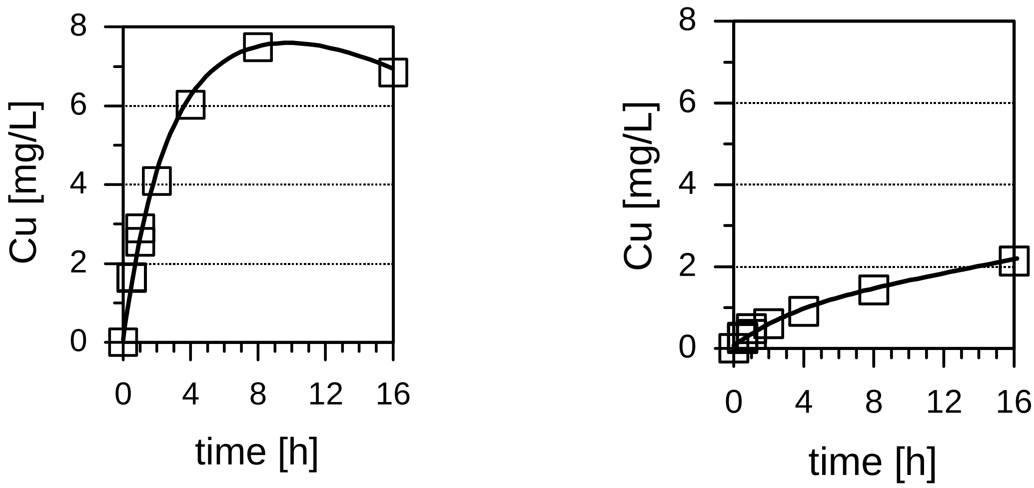

Figure 4: Stagnation curve for copper pipes charged with drinking water (left-hand side) and with drinking water containing 3 mg/L ortho-phosphate (right-hand side) after a running time of 26 weeks (water work 2)

Water work 3

The water of water work 3 has a total hardness of 20 °dH. The content of total organic carbon is between 2.0 and 2.5 mg/L and pH is about 7.2. Oxygen content is usually below 1 mg/L but sometimes was determined to be up to 2 mg/L. Therefore, this water quality is in contrast to the above mentioned ones especially because of the oxygen concentration.

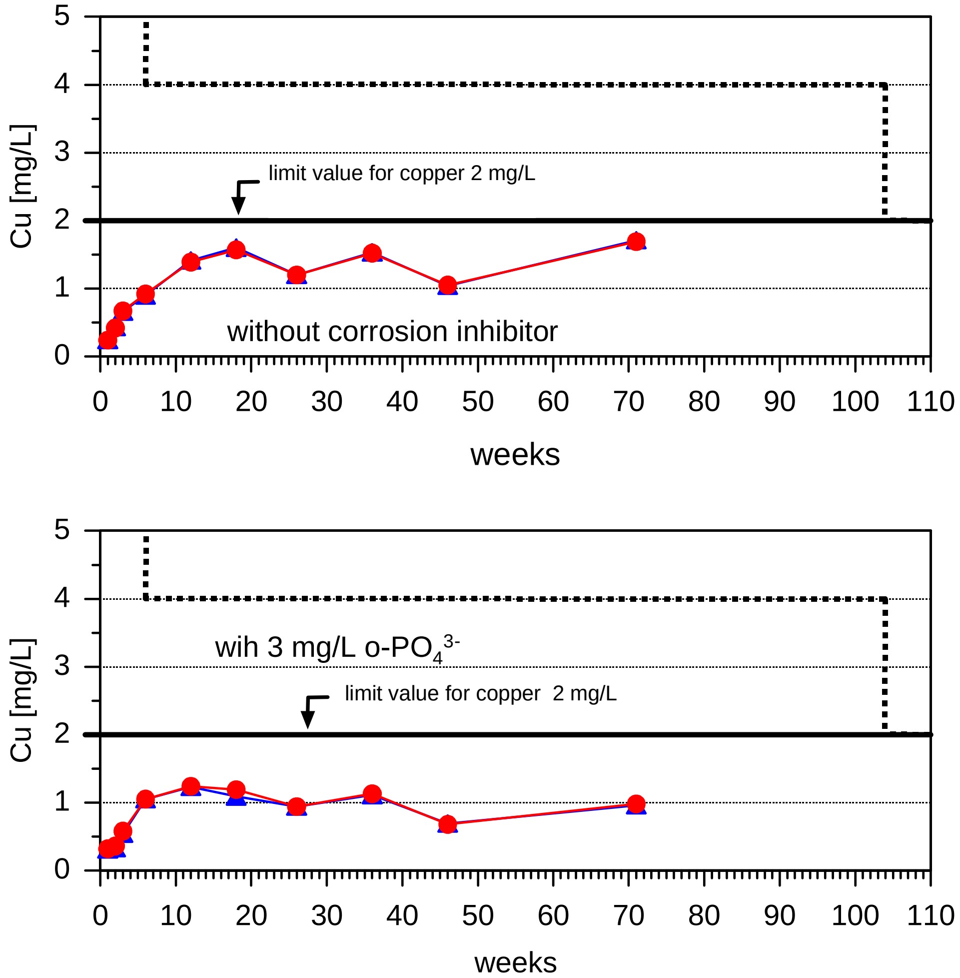

Figure 5: Mean values according to DIN 50931-1 in dependence of the running time determined within field test studies in water work 3

As can be seen in figure 5 the course of copper mean values according to DIN 50931-1 is totally different compared to the above mentioned field tests. Usually, copper mean values are increasing within the first 2 or 3 weeks and afterwards the values are constant or decreasing. But in this case the mean values are increasing within the first 20 weeks and afterwards they are varying between 1.0 and 1.5 mg/L. The field tests here demonstrate, that copper can be used in household installations although DIN 50930-6 gives restriction because of the water quality. Furthermore, if 3 mg/L ortho-phosphate are used as corrosion inhibitor copper release is not as far minimised as in the above presented cases. According to figure 5 copper mean values are still at 1 mg/L Cu after 1.5 years.

Again stagnation curves are given in figure 6 for a running time of 26 weeks. As can be seen for the delivered drinking water copper concentration is about 1 mg/L after a stagnation time of 0.5 hour and is not significantly changing with increasing stagnation time. The stagnation curve for the water containing 3 mg/L ortho-phosphate is slightly different because copper concentrations are increasing with increasing stagnation time and copper saturation takes place at roughly 4 hours and consequently copper concentrations remain constant until 16 hours of stagnation.

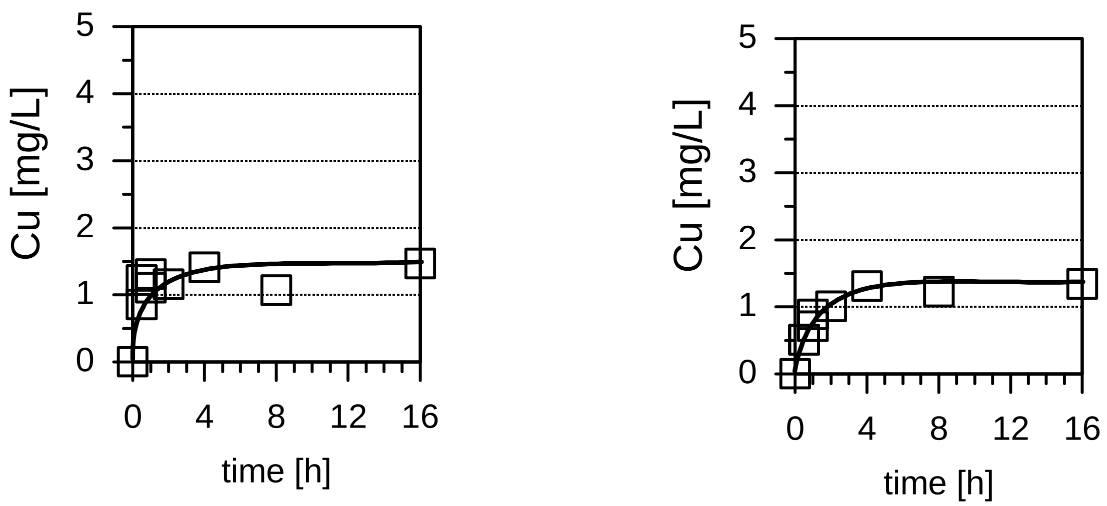

Figure 6: Stagnation curve for copper pipes charged with drinking water (left-hand side) and with drinking water containing 3 mg/L ortho-phosphate (right-hand side) after a running time of 26 weeks (water work 3)

4.2 Characterisation of the surface

With recent research activities it was found out, that copper release from copper pipes is mainly determined by the corrosion scales, which are formed on the copper pipe surface, and low copper concentrations in drinking water can be correlated to dense malachite layers [$CuCO_3$ $Cu(OH)_2$] [8]. Moreover, it was shown, that depending on the concentration and the origin organic carbon can retard or even prevent the formation of malachite on copper surfaces and therefore cuprite (Cu_2O) is the only identified crystal modification on the copper surface [9]. Nevertheless, the basic question still holds on how do ortho-phosphate effect the copper corrosion process. Therefore, after certain running times the inner surface of the copper pipes, which were installed in the test rigs, was investigated. In figure 7 the copper pipe surface after 26 weeks running time in water work 1 is presented.

As can be seen in figure 7 after 26 weeks running time on both surfaces no tight malachite layer is formed, which would be recognisable by its green colour. But remembering figure 1 without adding corrosion inhibitors copper release is quite high, while dosage of ortho-phosphate leads to a significant decrease of copper release. This result is confirmed when looking at the surfaces on the same copper pipes after 2.5 years running time, which are presented in figure 8. Although, one can clearly see, that on the pipe charged with drinking water a green layer was formed, malachite is not presented and the only identified crystal modification again is cuprite (Cu_2O). On the pipe, which was charged with drinking water containing 3 mg/L ortho-phosphate, also only cuprite (Cu_2O) is present, but regarding to the colour the cuprite layer is in contrast still almost red-brown. This effect is confirmed within further test rig experiments at different sites.

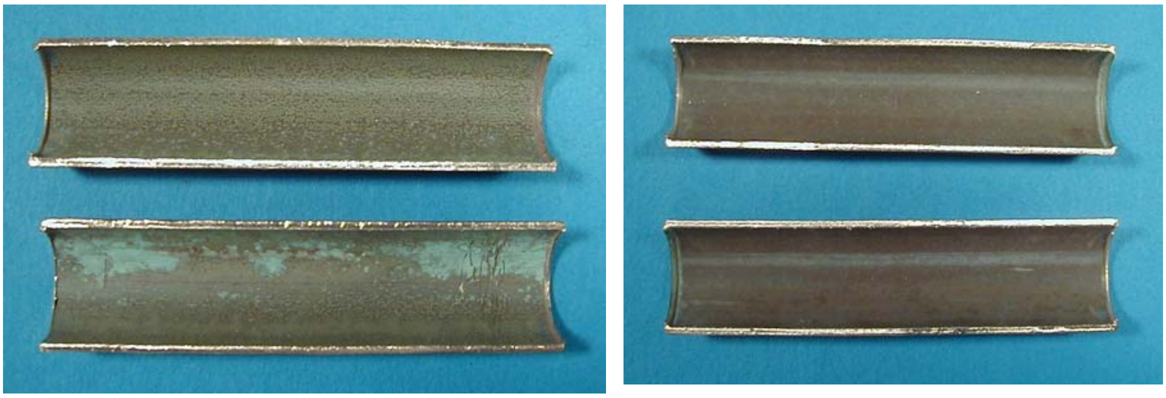

Figure 7: Copper pipe charged with drinking water (left-hand side) and with drinking water containing 3 mg/L ortho-phosphate (right-hand side) after a running time of 26 weeks (water work 1)

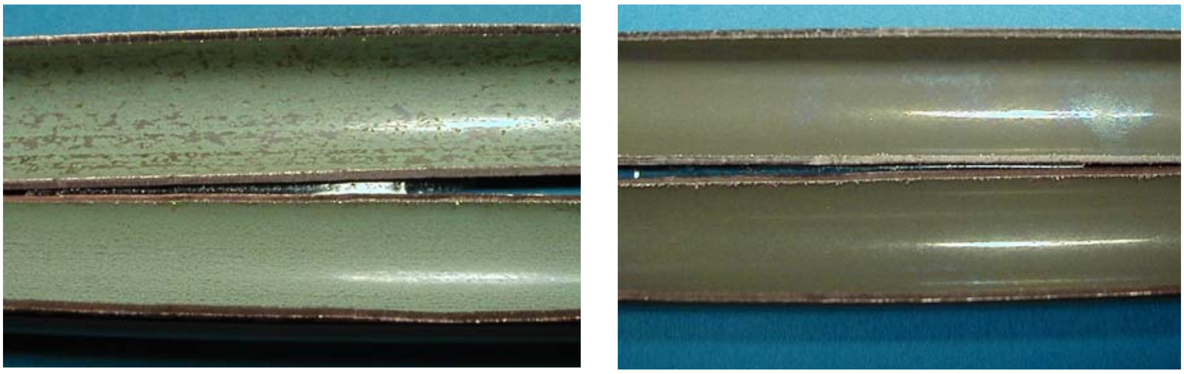

Figure 8: Copper pipe charged with drinking water (left-hand side) and with drinking water containing 3 mg/L ortho-phosphate (right-hand side) after a running time of 2 years (water work 1)

Because in both DOC and ortho-phosphate containing waters cuprite is the predominant crystal modification, but in contact with copper pipes only DOC containing waters are leading to high copper concentrations in the delivered water, in the case of ortho-phosphate other factors than the corrosion scale must be responsible for minimisation of copper release. Therefore, ortho-phosphate must directly affect the redox-reaction where copper plays the anodic and oxygen the cathodic part. This assumption is confirmed by experiments with model waters, which have shown that after ortho-phosphate is added oxygen consumption and consequently copper release is decreasing dramatically [9].

5 Conclusions

The results demonstrate that ortho-phosphate containing corrosion inhibitors influence the copper corrosion process, but at the moment it is not fully understood how they affect the redox process. Therefore, optimisation of corrosion inhibitors in respect to concentration and composition has to be done in practice case by case for each water quality. Future research activities will be focused on how corrosion inhibitors interfere with the copper corrosion reactions.

6 References

[1] Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption. Official Journal of the European Communities L 330 (1998), p. 32.

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