

# The influence of drinking water quality on corrosion processes and corrosion product formation

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## 1 Summary

Because of the definition of parametric values for copper and lead in drinking water investigations according to DIN 50931-1 were carried out with different water qualities. Whereas, the corrosion system of galvanised steel is well understood since years, the copper corrosion system and especially its influencing factors are not yet fully understood. With this paper some further findings in copper corrosion as well as results of recent experiments with galvanised steel are presented.

## 2 Introduction

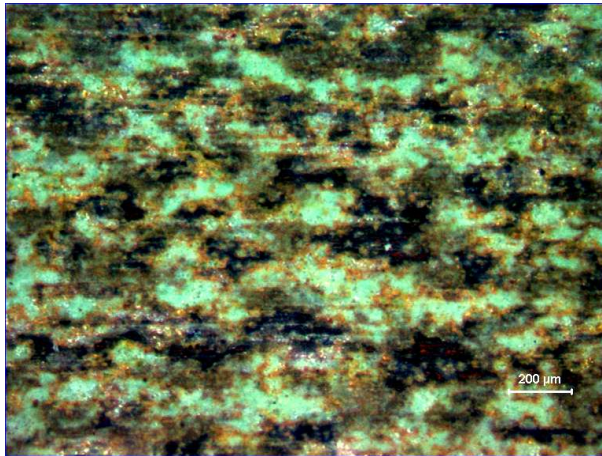
With the Council Directive 89/83/EC [1] the water quality at the consumers' tap became more important as before. Water quality is not only influenced by raw water quality and drinking water treatment but also especially by several other factors playing an important role during distribution to the consumers' tap. On its way drinking water comes into contact with different metallic and non-metallic materials. Whereas non-metallic materials can in principle alter drinking water quality mainly by leaching processes, metallic materials are subject to ongoing corrosion processes. These processes are dominated by the metallic material itself, by the consumption behaviour and also by the water quality. In order to study the effects of water quality on corrosion processes an unique model system has to be regarded, which simulates the consumption behaviour at consumers' tap. In Germany with DIN 50931-1 "Corrosion of metals – Corrosion tests with drinking water – Part 1: Testing of change of the composition of drinking water" [2] a suitable and comprehensive model system is described. Based on this standard test rigs were designed, which can be installed on-site at waterworks [3]. Metallic materials under investigation are mainly copper, galvanised steel and brasses as well as gun metals. In this paper results of investigations with copper and galvanised steel are presented.

## 3 Copper

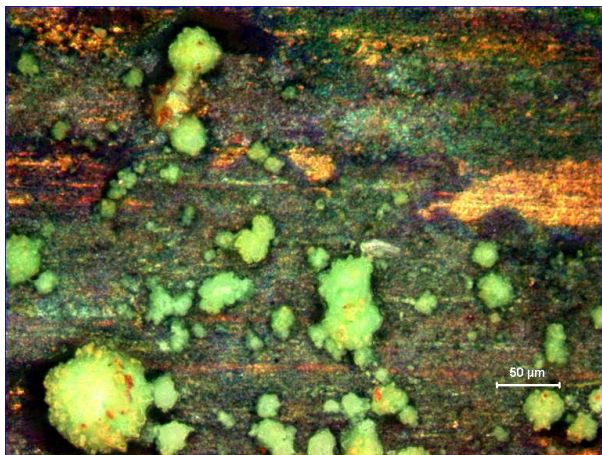
### 3.1 Corrosion layer

Copper corrosion and consequently copper release is influenced by many parameters as recent research activities have shown. One major point seems to be the potential of malachite [ $\text{CuCO}_3\text{Cu}(\text{OH})_2$ ] growth on the copper pipe surface [4]. Further investigations have demonstrated, that pH and natural organic matter (NOM) do mainly influence the formation of malachite. With higher concentrations of total organic carbon (TOC) malachite

formation is retarded or even prevented [5] and therefore copper release is quite high. But surface characterisation of various copper pipes has shown, that even in waters with comparatively high TOC contents turquoise green corrosion products could be found [6]. Because of these findings the question arised if theses corrosion products could be identified as malachite. Therefore, surfaces were characterised by x-ray diffraction, microscopy and additionally by infrared spectroscopy (IR). With x-ray diffraction using the General Area Diffraction Detection System (GADDS) malachite was not identified. This surprising finding was confirmed by the morphology of the corrosion layer. In picture 1 and 2 typically found corrosion layers are presented. As can be seen, the corrosion layers are amorphous and consequently quite different to the typical crystalline malachite structure.



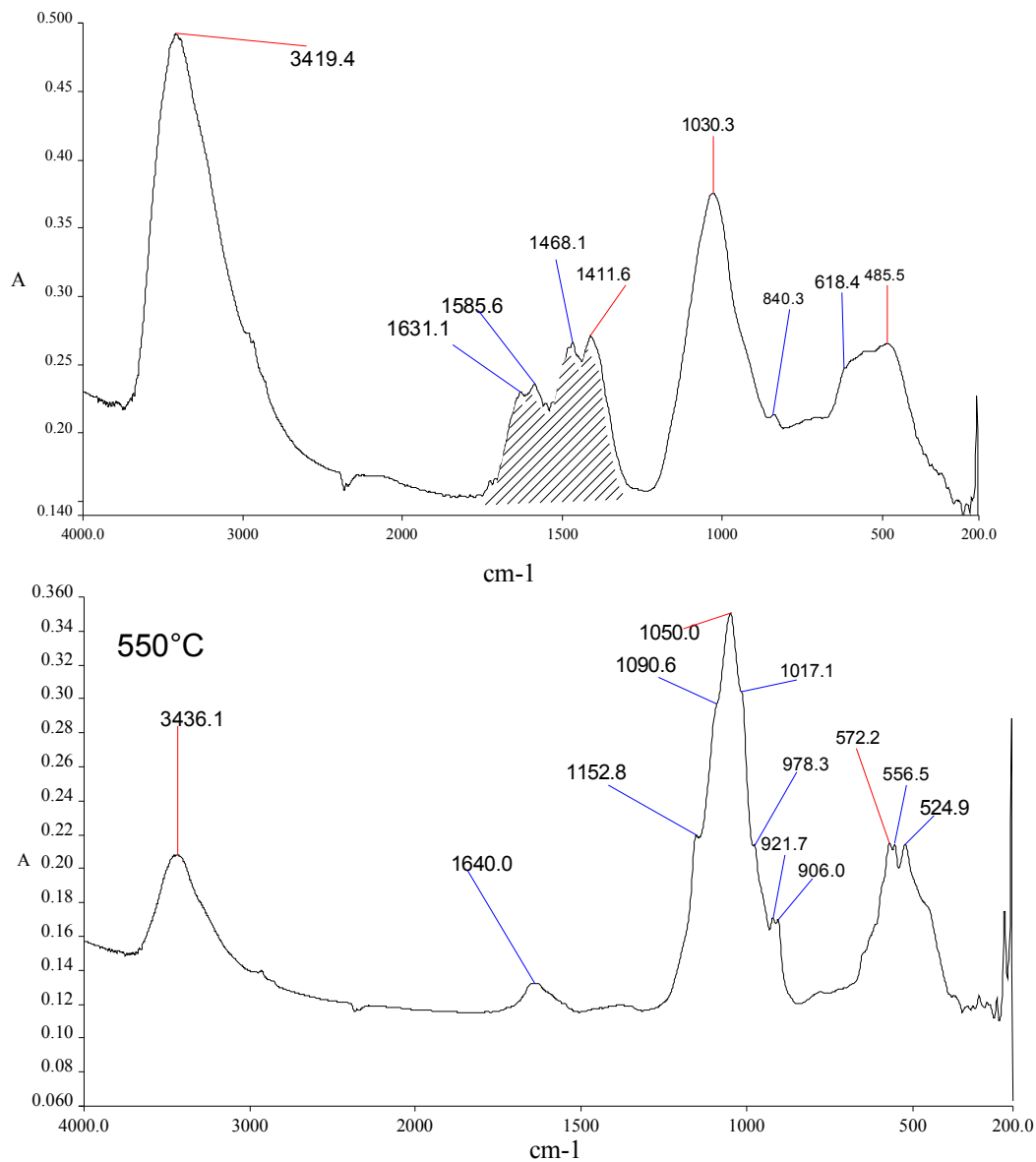
**Figure 1:** Morphology of a turquoise green copper corrosion layer – example 1.



**Figure 2:** Morphology of a turquoise green copper corrosion layer – example 2.

In order to identify the corrosion products further investigations were carried out. Selected corrosion layers were analysed by IR-spectroscopy. In figure 3 the IR-spectrum of a sample of an amorphous green corrosion layer before and after temperature equalization up to 550° C is given. As can be seen, the peaks around 1500 cm<sup>-1</sup>, which belong to malachite, almost disappeared after the sample was treated with high temperature and simultaneously the peaks around 550 cm<sup>-1</sup> belonging to CuO were increasing [7]. This means, that the formed

green corrosion products can be regarded as a type of amorphous malachite. Additionally, this finding could be confirmed by measuring the carbonate content of the copper corrosion layer. Therefore, a special analytical techniques was developed and introduced.

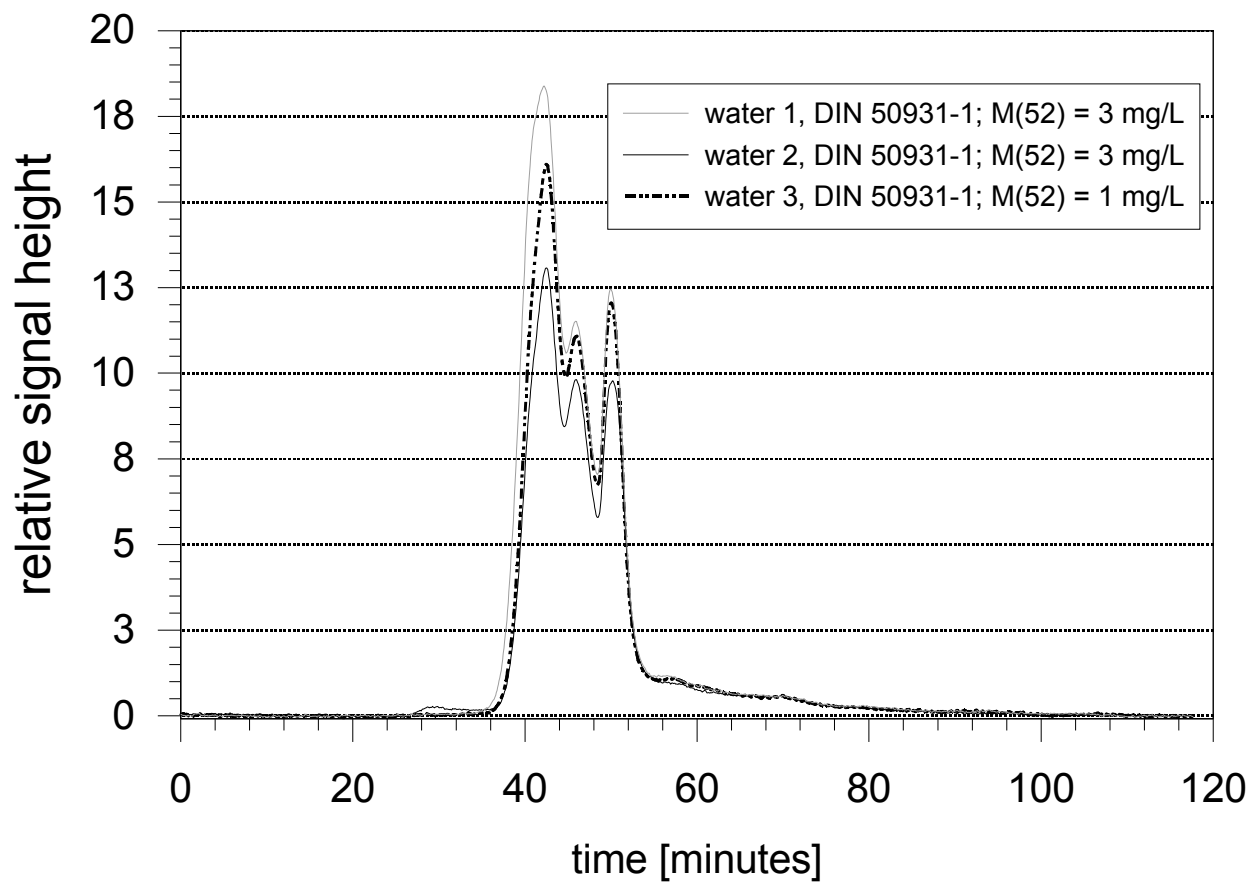


**Figure 3:** IR spectrum before and after temperature equalization of a turquoise green corrosion layer [7]

### 3.2 Water quality

Especially in waters with pH around 7.4 the influence of organic carbon content on copper release and on malachite formation can be verified. But it is not yet identified how NOM do interfere the copper corrosion system and which attribute of NOM is responsible for the caused effects. Therefore, three different waters with almost the same chemical-physical properties as well as comparable TOC concentrations were used and experiments according to DIN 50931-1 were carried out. The pH of the regarded waters was between 7.2 and 7.4

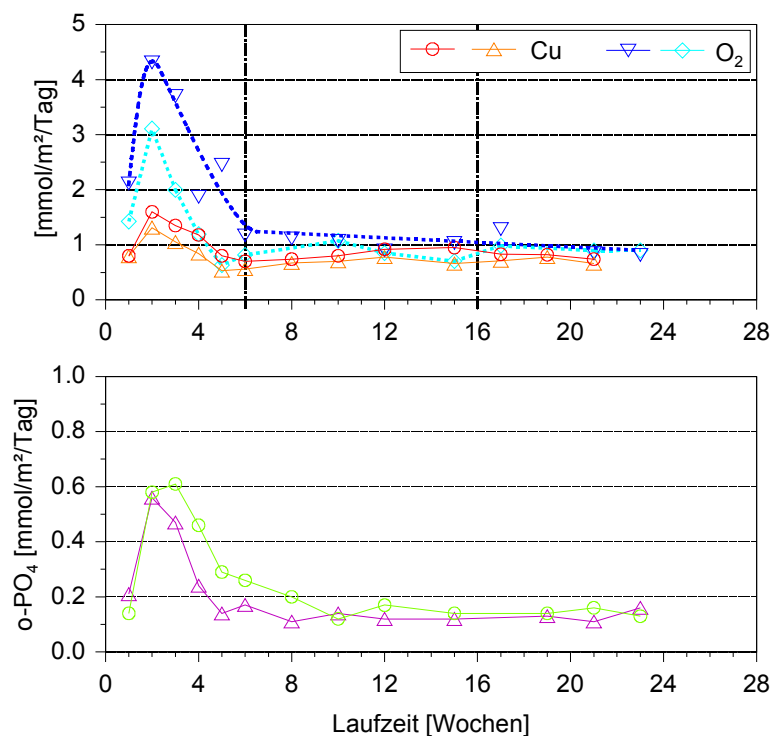
and TOC values varied between 2.0 and 2.5 mg/L. Copper release was determined to 3 mg/L for water 1 and 2 and to 1 mg/L for water 3. Because the water qualities were almost comparable the nature of NOM might be responsible for the different behaviour in respect to copper release. Therefore, NOM characterisation was done by gel-chromatography and results are given in figure 4. As can be seen, besides of the peak height there is no significant difference, which can explain the findings mentioned above. This might be attributed to the fact, that gel-chromatography is based on size distribution only. This means, that other methods for TOC characterisation are needed, with which e.g. the complexation and adsorption behaviour of NOM in interaction with copper can be described. Future research activities will focus on this.



**Figure 4:** Gel-chromatogram of three different waters, which cause different amount of copper release

Besides of NOM it is also well known, that ortho-phosphate does influence the copper corrosion system [6, 8]. Especially, in case of high copper release the addition of ortho-phosphate caused decreasing copper concentrations. As recent research work has demonstrated simultaneously with the introduction of ortho-phosphate dosage the total corrosion process is dramatically diminished [5], which is proofed by the oxygen consumption. Studies in the past concluded, that ortho-phosphate is adsorbed on the copper surface and therefore the oxidation process is hindered [9]. For that reason, first experiments were carried out in order to study if a certain phosphate consumption can be

observed. But results were not very uniform. Consequently, model experiments according to DIN 50931-1 were started and besides of copper release, oxygen and ortho-phosphate consumption were determined. The regarded water quality and the obtained results are given in figure 5, in which all results are calculated to the unit  $\text{mmol}/(\text{m}^2 \text{ d})$ . As can be seen, in the first six weeks of operation copper values are at the highest and thereafter values are almost constant. Moreover, at the beginning oxygen consumption is higher than copper release. This means, that a corrosion layer should be formed. After six weeks operation oxygen consumption and copper release are almost equivalent. In the lower part of figure 5 ortho-phosphate consumption is shown and again consumption is at the highest in the first weeks. Consequently, it can be assumed that a certain amount of ortho-phosphate is fixed as a copper-phosphate compound. But this compound is formed only, if copper concentration is high enough. This assumption can be confirmed with figure 6, in which copper and phosphate concentration at different stagnation times are given. On the right hand side of figure 6 an almost linear correlation between copper and ortho-phosphate can be seen. This means, that in the system copper/ortho-phosphate/drinking water also precipitation has to be regarded.

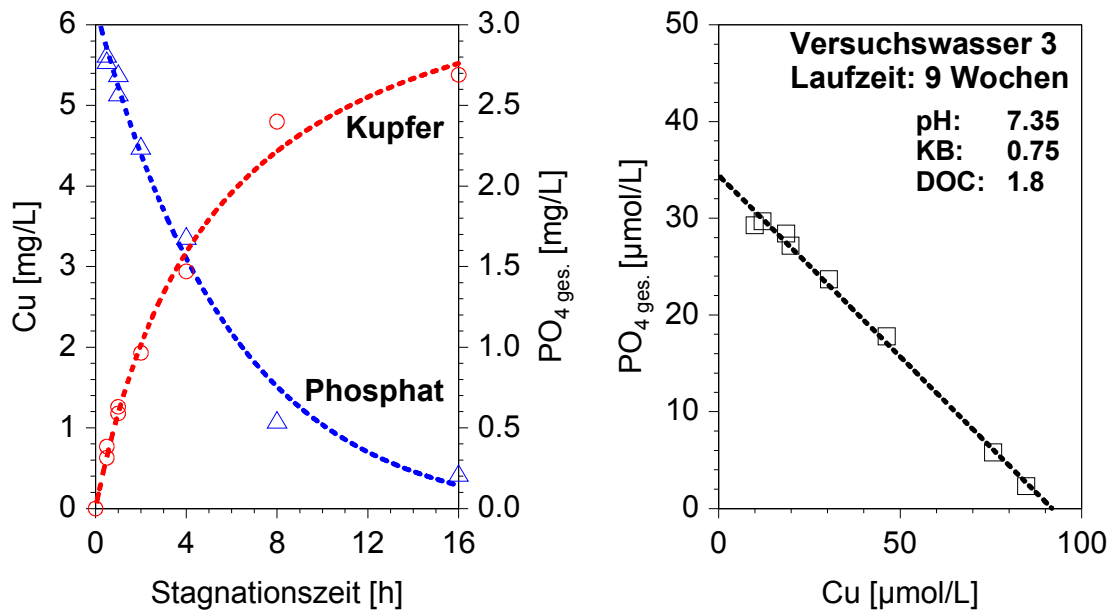


### Water Quality

pH		7,2
KB <sub>8,2</sub>	[mmol/m <sup>3</sup> ]	0,9
KS <sub>4,3</sub>	[mmol/m <sup>3</sup> ]	5,3
Ca	[mg/L]	120
Na	[mg/L]	20
SO <sub>4</sub>	[mg/L]	60
Cl	[mg/L]	45
NO <sub>3</sub>	[mg/L]	10
DOC	[mg/L]	1,5
o-PO <sub>4</sub>	[mg/L]	3,0

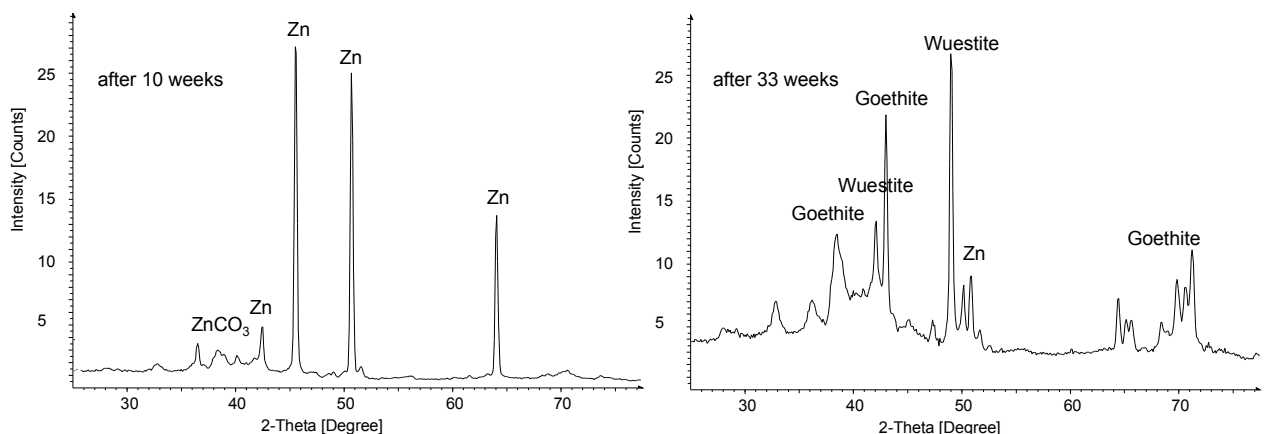
**Figure 5:** Experiments according to DIN 50931-1

**Figure 6:** Interrelationship between copper and ortho-phosphate



#### 4 Galvanised steel

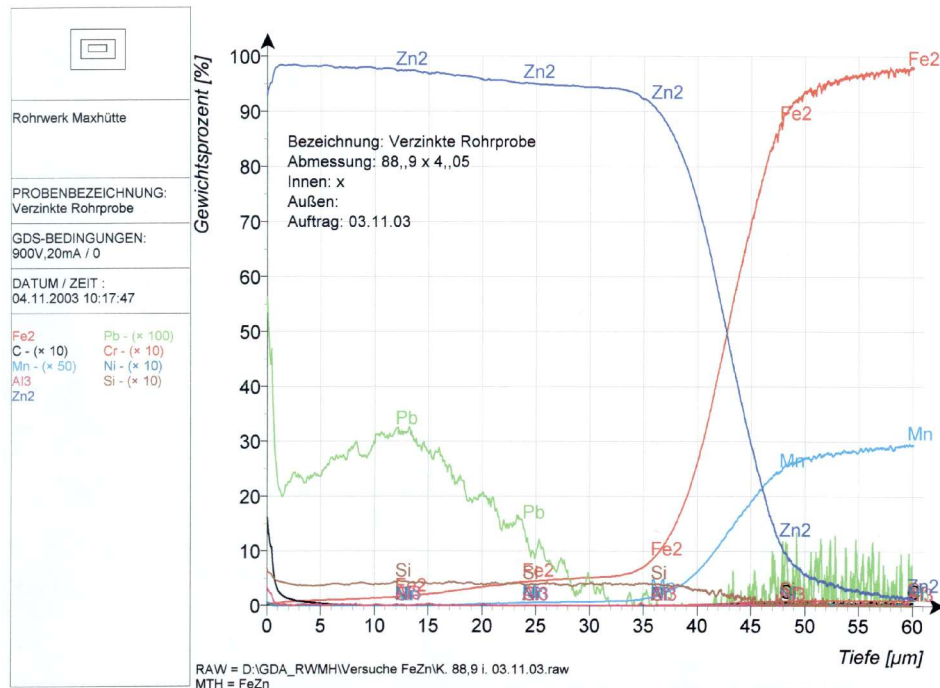
The corrosion processes taking place with galvanised steel are well understood. Main parameters influencing the corrosion system are pH of the water and flow velocity. Moreover, the zinc layer is a temporary corrosion protection and therefore after sufficient operation time one has to regard the iron corrosion system of the base steel [10]. This known behaviour is also verified within experiments according to DIN 50931-1, which were carried out in order to quantify lead release in dependence of different water qualities. In figure 7 the corrosion layer was investigated by x-ray diffraction. On the left hand side corrosion layer after 10 weeks operation time and on the right hand side after 33 weeks operation time using a water with pH 6.5 is presented. As can be seen the longer the operation time the more iron corrosion products are identified.



**Figure 7:** Corrosion layers on galvanised steel pipes after different operation times within experiments according to DIN 50931-1

As experiments with different water qualities have shown, the amount of lead release is mainly dominated by the lead content in the zinc layer. Whereas, in the past lead content

was about 0,8 % nowadays lead content is below 0,25 %. A typical lead distribution characteristic is given in figure 8 [12]. Because of the requirements given by DIN 50930-6 [11] in the meantime many manufactures are able to produce galvanised steel pipes with lead contents below 0,1 %.



**Figure 8:** Distribution characteristic of a zinc layer

## 5 Conclusions

Concerning copper corrosion further research will be carried out in order to identify how NOM and corrosion inhibitors like ortho-phosphate effect the copper corrosion system. Experiments according to DIN 50931-1 with galvanised steel can be carried out in order to decide whether or not lead release from galvanised steel pipes will cause non-compliance in respect to the drinking water limit value for lead of 10 µg/L.

## 6 References

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