

**Optimisation of a drinking water corrosion inhibitor
with special regard to
electrochemical investigation in field studies**

*Angelika Becker, Ute Ruhrberg, Timo Jentsch, IWW Water Centre,
Mülheim an der Ruhr, Germany*

*Wolfgang Hater, Peter Schmidt, BK Giulini GmbH, Ludwigshafen, Germany
Alexander Garweg, Stadtwerke Bad Hersfeld GmbH, Bad Hersfeld, Germany*

Contact:

IWW Water Centre
Moritzstrasse 26
45476 Muelheim an der Ruhr
www.iww-online.de

t.jentsch@iww-online.de
a.becker@iww-online.de
u.ruhrberg@iww-online.de

*BK Giulini GmbH
BKG Water Solutions
Giulinistraße 2
67065 Ludwigshafen
www.bkgwater.com*

*Peter.schmidt@bk-giulini.com
Wolfgang.hater@bk-giulini.com*

*Stadtwerke Bad Hersfeld GmbH
Kleine Industriestraße 1
36251 Bad Hersfeld
www.stadtwerke-hef.de*

garweg@stadtwerke-hef.de

Summary

Drinking water treatment with corrosion inhibitors based on phosphate or silicate 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. Red water is a term for water with high particulate iron concentrations due to corrosion by-product release.

Besides water quality, the type and concentration of the inhibitor added as well as the material to be protected influence the efficiency of corrosion inhibition. Practical experiences show that optimising the composition of a corrosion inhibitor and its concentration in drinking water is only possible by testing the system in test rigs to get reliable data for decision-making.

To test the iron uptake into the water in general a closed circuit system is used to determine the oxygen depletion and thus corrosion rate. With this method – based on the assumption that there is a direct correlation of the oxygen depletion and the iron uptake due to the corrosion process – it is possible to determine the iron uptake rate of waters in contact with new or scaled iron pipes. The combination of this method with mass loss measurements as well as investigation of the iron layer concerning chemical composition and scale morphology gives additional information of the characteristics and the protection properties of the iron layer.

But, this kind of investigation did not give detailed information on corrosion mechanisms due to the characteristics of the corrosion inhibitor which may function as an anodic, a cathodic or a mixed anodic-cathodic inhibitor.

This paper will focus on a three years field study to optimise the composition of the inhibitor (replacement of a pure phosphate with a phosphate/silicate combination product) and its concentration in drinking water with special respect to electrochemical investigation. Based on current potential characteristics information of layer resistance and its protective function with respect to the inhibitor components phosphate and silicate are presented.

The results show that in the tested drinking water the concentration of the pure phosphate inhibitor can be minimised – by equal corrosion protection – from a concentration of 4 mg/l PO_4 to a concentration of 0.6 mg/l PO_4 , if additionally a silicate inhibitor is used. With respect to the water quality 6 mg/l SiO_2 was sufficient. In the sequence pure phosphate – phosphate/silicate – pure silicate it was possible to succeed in a comparable corrosion protection by use of an activated silicate inhibitor.

1 Introduction

The maintenance of water distribution systems is essential to protect water quality. One of the main influencing factors is the corrosion behaviour of the installed pipe and fitting materials while interacting with the drinking water due to its corrosion properties. Frequently mentioned customer complaints are problems with discolouration or with the occurrence of red water. Apart from the noncompliance with the

drinking water directive (limits for iron concentration, turbidity) optical problems with red water lead to a significant loss of image of the water company. To avoid these problems the dosage of corrosion inhibitors based on phosphate or silicate is a common method [1; 2; 3].

But practical experiences show that optimising the composition of a corrosion inhibitor and its concentration in drinking water is only possible by testing the system in test rigs to get reliable data for decision-making [2; 3].

On behalf of a water company in Germany, investigations in test rigs should be done to review the possibility to reduce the amount of the phosphate concentration in the drinking water and to check economical savings by equal corrosion protection. The main reason to implement corrosion tests was originated in the requirement of the local health authority to minimise the phosphate content in the drinking water. The dosage of a drinking water corrosion inhibitor while distributing a varying drinking water quality results in mixing zones of the water supply network. For the purpose of corrosion protection in drinking water networks only products based on phosphate and silicate comply with the drinking water directive. The limited concentration in drinking water after treatment in Germany is 6.7 mg/l PO₄ and 15 mg/l SiO₂ [4; 5].

The corrosion behaviour of steel pipes was studied in field tests over a period of three years.

2 Methods and experiments

2.1 Electrochemical methods

Corrosion of iron or cast iron in drinking water systems is an electrochemical process which can be divided into a cathodic part and an anodic part of the chemical reaction. The anodic part is the dissolution of iron (2.1). The cathodic part is the reduction of oxygen (2.2).

- anodic partial reaction: dissolution of iron



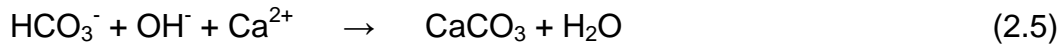
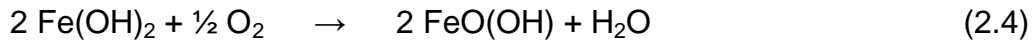
- cathodic partial reaction: reduction of oxygen



In the anodic reaction metal atoms are ionised and pass into solution leaving their electrons within the original metal surface. In the cathodic reaction the free electrons within the metal are taken up by oxygen in reduction reactions. In neutral to alkalised solutions oxygen will be reduced to hydroxyl-ions (OH⁻).

By hydrolysis of iron-ions as the resulting secondary reaction at the anode metal hydroxides or oxides are built (equations 2.3 and 2.4). An exemplarily consecutive reaction at the cathode using water content agents is the formation of calcium carbonate (2.5).

- some consecutive reactions:



These and other corrosion products adhere on the metal surface and due to their quality structure and properties inhibit or stimulate ongoing corrosion processes. Inhibition will be present if the mass and charge transport through the corrosion layer is significantly interfered.

The conditions for precipitation and stabilisation of the layer will be generated by one or both partial reactions. Therefore the position of precipitation will be determined by the kinetic of the chemical consecutive reaction. The anodic process of metal solution and the cathodic process of reduction of an oxidising agent are electrically connected and take place with the same velocity but locally separated on the material surface. So in doing, an electronic current must flow through the metal and a current must flow in electrolytes by ion transport.

Equations 2.1 and 2.2 indicate also that the primary partial reactions of corrosion are always associated with a charge transfer (ion or electron) through the phase boundary. That means that currents can be detectable whereas the intensity is affected by the electric resistance at the phase boundary. Classical electrochemical measurements amount principally to get information about the layer resistance and thereby about the activity of the corrosion system. An established procedure is the measurement of current potential curves. The first step is in general the determination of the free corrosion potential. With respect to similar conditions – for example regarding pH, oxygen content, temperature, flow velocity – the corrosion potential characterises in the first approximation the driving force of the corrosion reaction. The more reactive the metal the more negative is its standard potential. The less noble the metal the more tendentious its dissolution might be.

For electrochemical investigation different methods are available.

The selection of the method is determined by the target of the investigation. For the measurements described in the present paper the typically used three electrodes cell consisting of working electrode, reference electrode and counter electrode is modified in double performance of ring samples [6].

The chosen method of galvanodynamic polarisation depends on the fact that by applying a continuously increasing current a detectable changing of the potential can be measured. By application of these results current potential curves are generated. Its behaviour gives information of the resistance of the surface layer and its protective characteristics.

2.2 Corrosion rates and iron uptake

For investigations to assign iron uptake into water, a closed circuit system is used to determine the oxygen depletion and thus corrosion rate. Based on the assumption

that there is a direct correlation of the oxygen depletion and the iron increase due to the corrosion process it is possible to calculate the actual corrosion rate by considering the corroding iron surface and the water volume with respect to flowing conditions.

For the measurement itself (see figure 1), water is pumped through the test pipe with respect to the same conditions which are realised in the main test rig (water temperature, water quality, flowing conditions etc). As a result of the corrosion process the oxygen concentration of the water decreases and the iron content in the flowing water increases. While the oxygen concentration is measured in situ the increase of iron content is monitored by analysing samples. With this method it is possible to determine the iron uptake rate of waters in contact with new or scaled pipes.

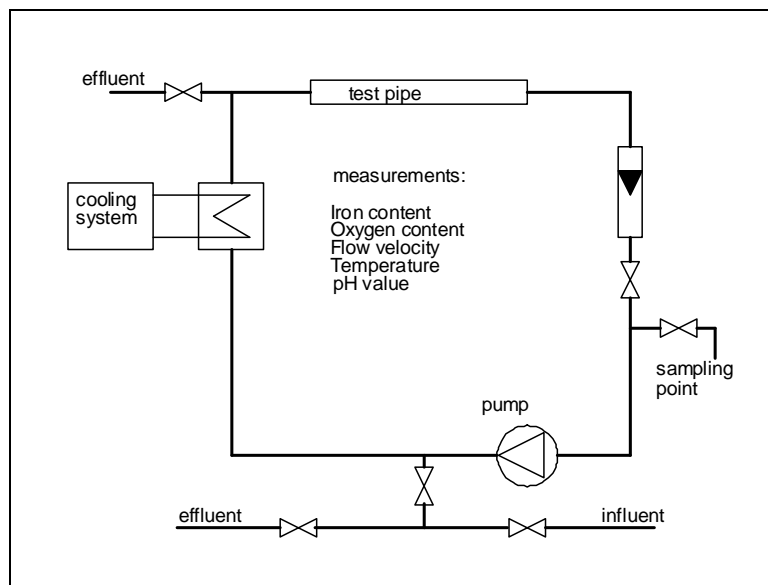


Figure 1: Investigation loop (closed circuit measurement system)

2.3 Corrosion rates and layer characteristics

For determining the corrosion rate by the ring column method prepared iron samples are flowed through by the tested water for a defined period of time and the weight loss during this time was measured (each iron ring is numbered, pickled and the weight is documented before exposure). The weight loss is normalised by the sample area in order to determine corrosion rates.

For measurement of thickness and chemical composition the iron samples are weighed after being demounted from the test rig and before being pickled for weight loss measurements. The acid using for pickling was analysed to get information about the chemical composition of the iron layer.

2.4 Experimental design

Figure 2 shows the experimental design. Three parallel operating test rigs with pipes of 20 mm diameter made of unalloyed steel were installed directly in the building of the water supply works. They could be admitted by the original drinking water as well

as by inhibitor dosed water qualities. The test rigs were continuously flowed through with water.



Figure 2: Three parallel test rigs

Details of the test rig are presented in figure 3. Pipes of 1 m length (a) were followed by pipes of 20 cm length (b) and by columns of ring segments of 20 mm length for mass loss measurements and detailed chemical and morphological scale investigation (c) and for electrochemical investigation (d).

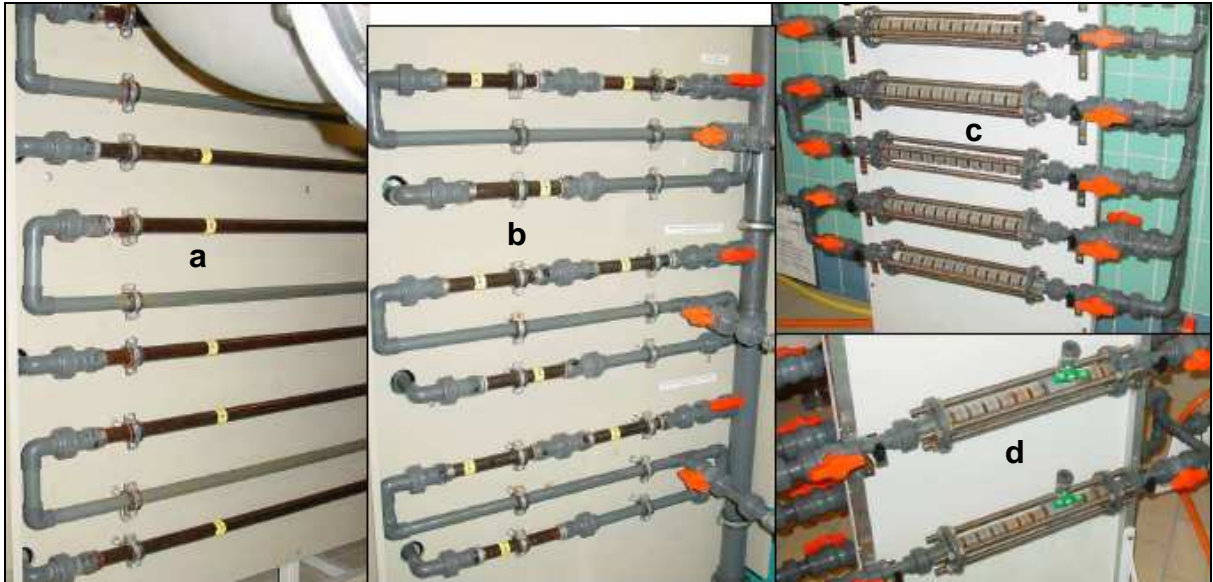


Figure 3: Test rig details

2.5 Test execution

2.5.1 Corrosion inhibitors

For investigation two different drinking water inhibitors were used. The phosphate inhibitor was a combination product of 75 % ortho- and 25 % poly-phosphate. The silicate inhibitor was carbonate activated in combination with caustic soda and sodium hydrogen carbonate.

2.5.2 Test water

The test idea can be described by the distribution of the different test waters (figure 4). One of the test rigs was operated with the untreated drinking water without inhibitor as reference. During the first year both other test rigs were operated with the treated drinking water with a phosphate concentration of 4 mg/l PO₄ to reach a comparable state of the surface layer like in practice. After a period of one year, in test rig 3 the inhibitor composition was changed to 0.6 mg/l PO₄ and 6 mg/l SiO₂. After a period of nearly 3 years in test rig 2 the inhibitor was changed to a pure carbonate-activated silicate inhibitor in a concentration in drinking water of 8 mg/l SiO₂.

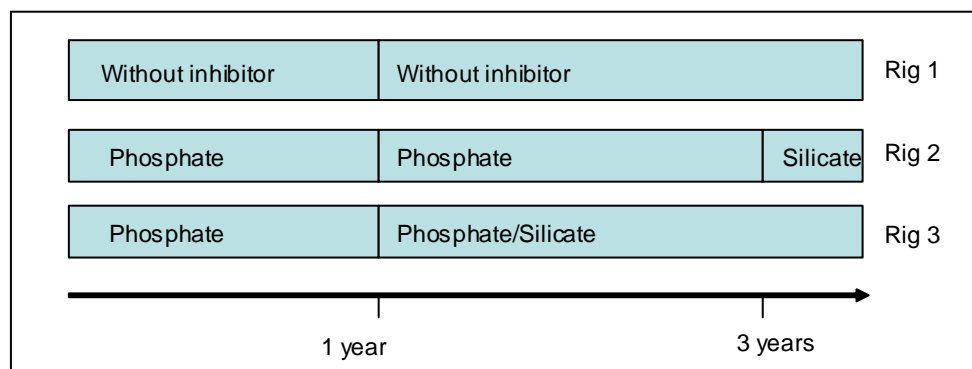


Figure 4: Test concept

The test rigs were operated with only continuous flowing conditions.

3 Results

3.1 Corrosion rates

Figure 5 shows the results of the corrosion rate measurement using the closed circuit test loop. Firstly the results show great variation in the data which show sensitivity for changing in the operation conditions due to the changing in the oxygen concentration within the tests in the closed circuit loop. The pipes operated with the drinking water without inhibitor show the highest corrosion rates over the whole test period. The best corrosion protection is determined by the test pipes of test rig 3 when the inhibitor was changed from pure phosphate to phosphate/silicate.

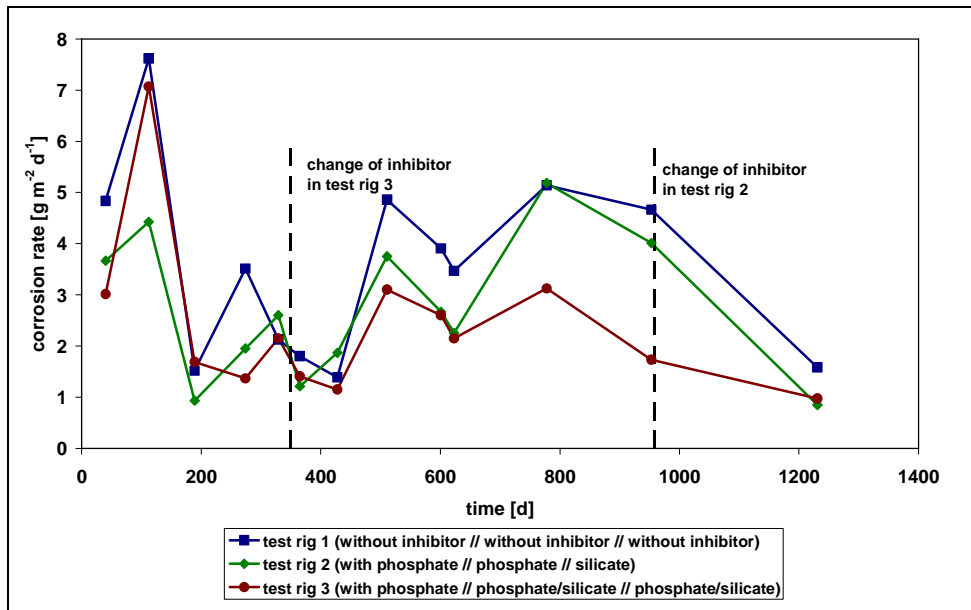


Figure 5: Corrosion rates by oxygen depletion

3.2 Mass loss and iron layer characteristics

Figure 6 shows the results of the mass loss measurements which describe the total loss of iron-material within the corrosion process. The test results show that the mass loss is far smaller by treating the water with inhibitor. The estimation of the data and the trend of the curves show that the changing of the inhibitor from pure phosphate to phosphate/silicate lead to the same corrosion protection.

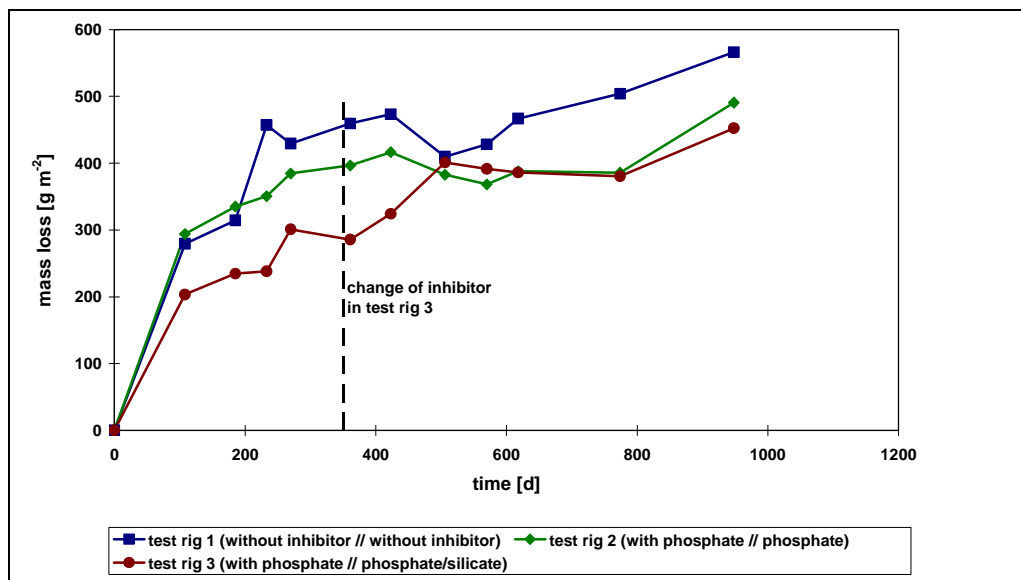


Figure 6: Mass loss measurements

Additionally the thickness and morphology of the iron layer was investigated. Figure 7 shows the results. The data show that differences in the development of the iron layer can only be determined between the iron samples operated without inhibitor and the samples operated with changing inhibitor composition in test rig 3. But these data could not give an answer to the protection characteristics of the iron layer.

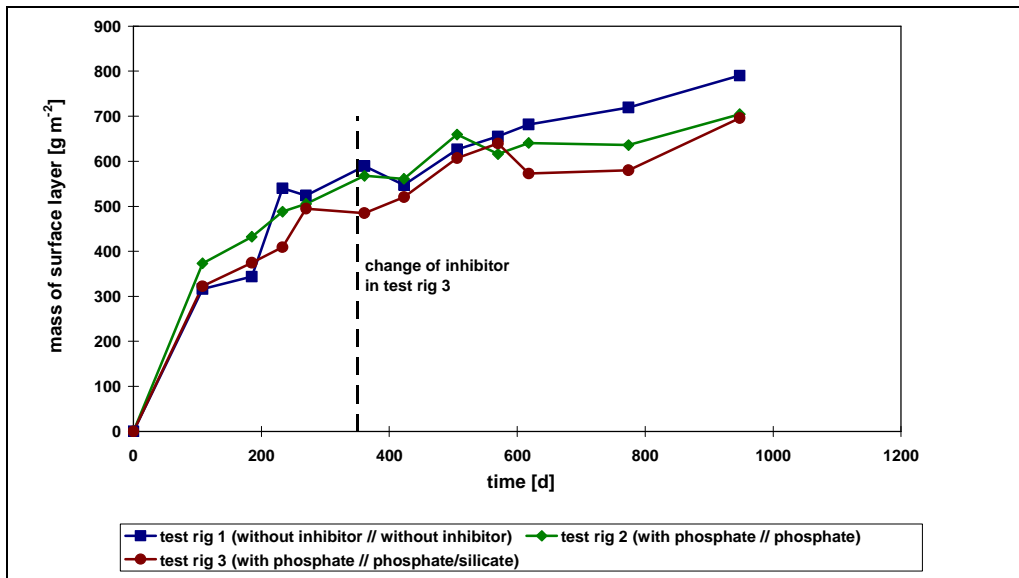


Figure 7: Mass of iron surface layer

For this assessment examinations of the morphology and electrochemical investigations were necessary.

Figure 8 shows examples of the morphology of the iron surface layer in dependence of the water composition. It is clearly visible that the surface layer, which was built in the drinking water without inhibitor dosage, tends to a non-uniform corrosion with forming of rust tubercles. In contrast to this the layer built in the inhibitor-treated test-water shows uniform appearance with higher protective properties.

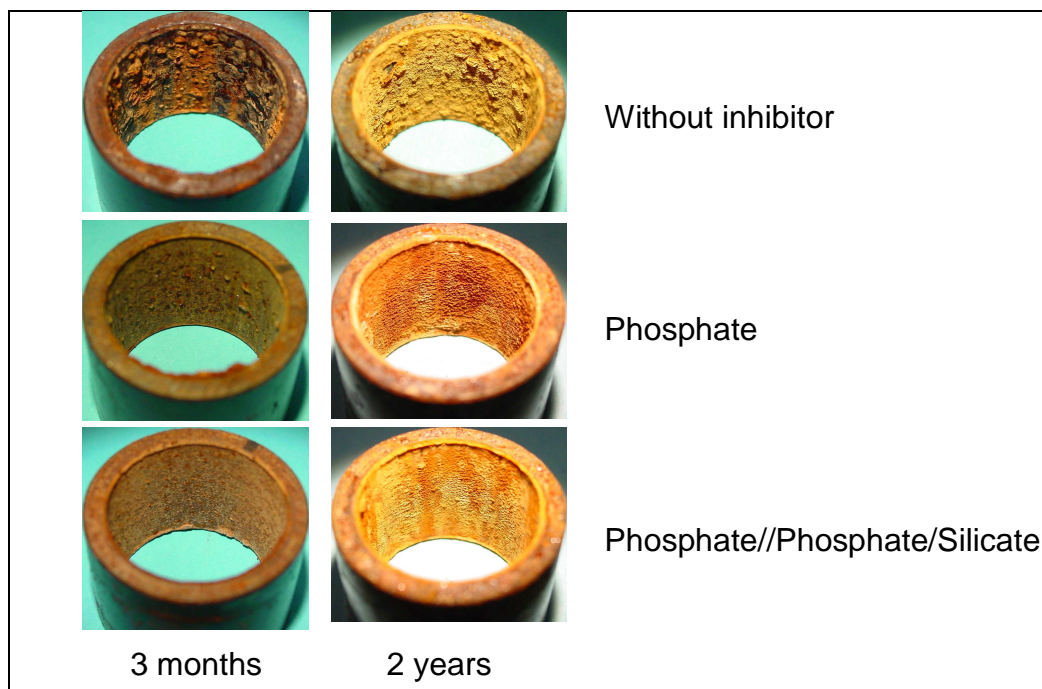


Figure 8: Development of the surface layer

3.3 Electrochemical investigation

All electrochemical measurements were done while water was flowing through the ring specimen columns. So the system was investigated while in use.

After measurement of the free corrosion potential E_{corr} for 30 minutes and after being sure that it remains constantly at the same value, the working electrodes were impinged firstly by cathodic polarisation. A day later – for recovering the free corrosion potential – anodic polarisation was performed.

The development of the surface layer can be observed by regarding the time dependence of the slope of the current potential curves. Exemplarily a significant flattening is visible in the cathodic polarisation curves in figure 9. Equal amounts of polarisation current result in higher shifts of the electrochemical potential – the elder the layer the greater the potential shift. That indicates a growing surface layer with increasing homogeneity and density, therefore with increasing corrosion protection feature.

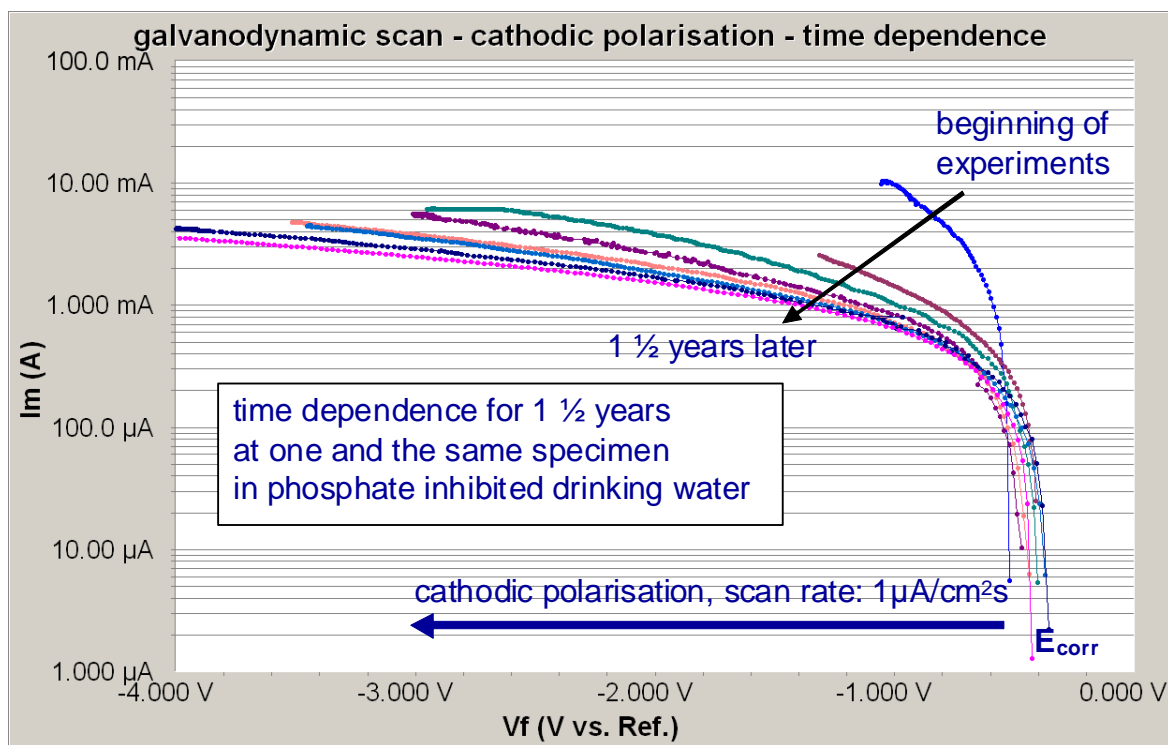


Figure 9: Time dependence for 1 ½ years

The comparison of current potential curves of the three systems which were treated parallel, but with different inhibitor compositions show the difference in corrosion protection capability of the developed surface layers.

During the first 10 months of operation time one test rig was operated without inhibitor, the other both had been treated by inhibitor dosage of a phosphate based inhibitor. There was a distinct difference visible between the system without inhibitor and the systems with the phosphate inhibitor. Both polarisation curves – cathodic and anodic polarisation – show a clear flattening of the slope (figure 10). The inhibitor is

definitely effective due to the incorporation of calcium-phosphate and iron-phosphate into the surface layer.

Beside that it is obvious that the inhibitor acts as a mixed anodic-cathodic inhibitor, but with a considerable stronger efficiency at the cathodic side.

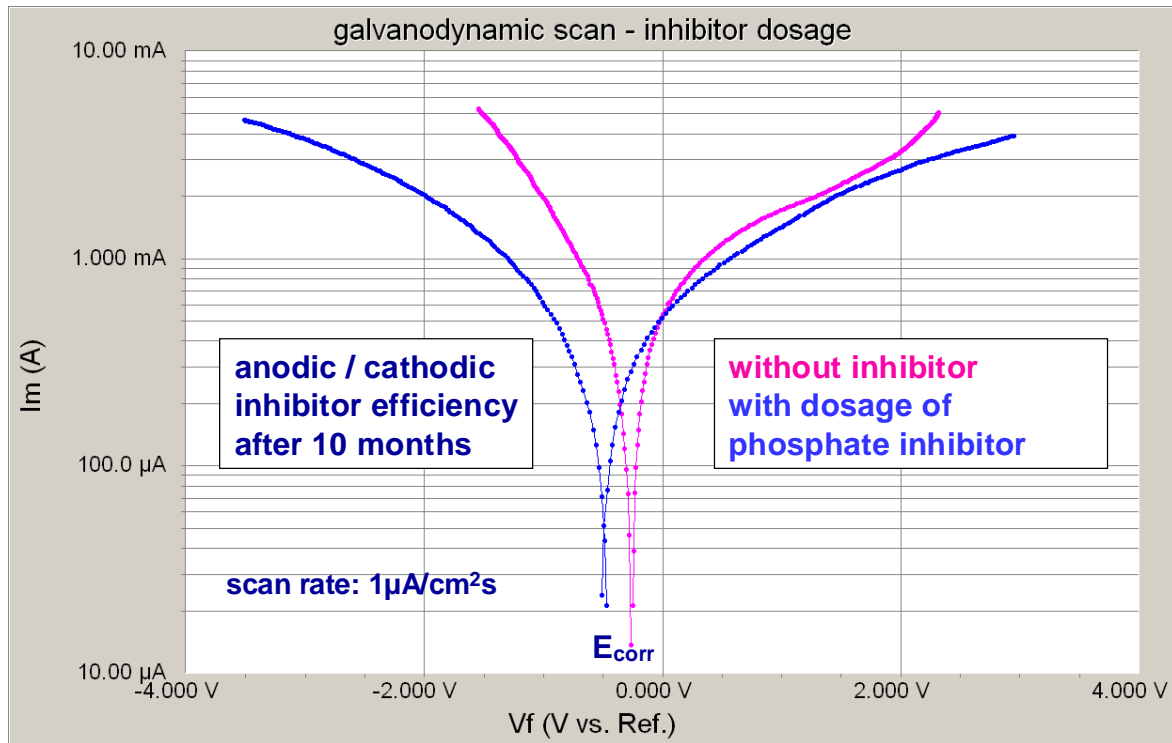


Figure 10: Inhibitor efficiency

To proof an optimisation of the inhibitor composition one of the inhibitor dosed test rigs got a change in the inhibitor composition of the test water. The phosphate based inhibitor (4 mg/l PO_4) was replaced by an inhibitor which contents much less phosphate (0.6 mg/l PO_4) and carbonate-activated silicate (6 mg/l SiO_2).

After only a few weeks of operation time there was a distinct effect visible (figure 11). The slope of the cathodic current potential curve of the samples of the phosphate/silicate inhibited test rig was a little bit smaller than the one of the phosphate inhibited test rig samples, corresponding to a slight difference in the cathodic corrosion protection properties of the surface layer.

But the slope of the anodic current potential curve of the phosphate/silicate inhibited test rig samples was enormously smaller. Therefore the anodic efficiency of the phosphate/silicate inhibitor is much bigger than of the pure phosphate inhibitor.

The combined phosphate/silicate inhibitor acts as an obviously balanced mixed anodic-cathodic inhibitor. The surface layer could incorporate the new inhibitor molecules although the time was rather short. The restructured layer with the new inhibitor involved was quite efficient protecting the surface from corrosion.

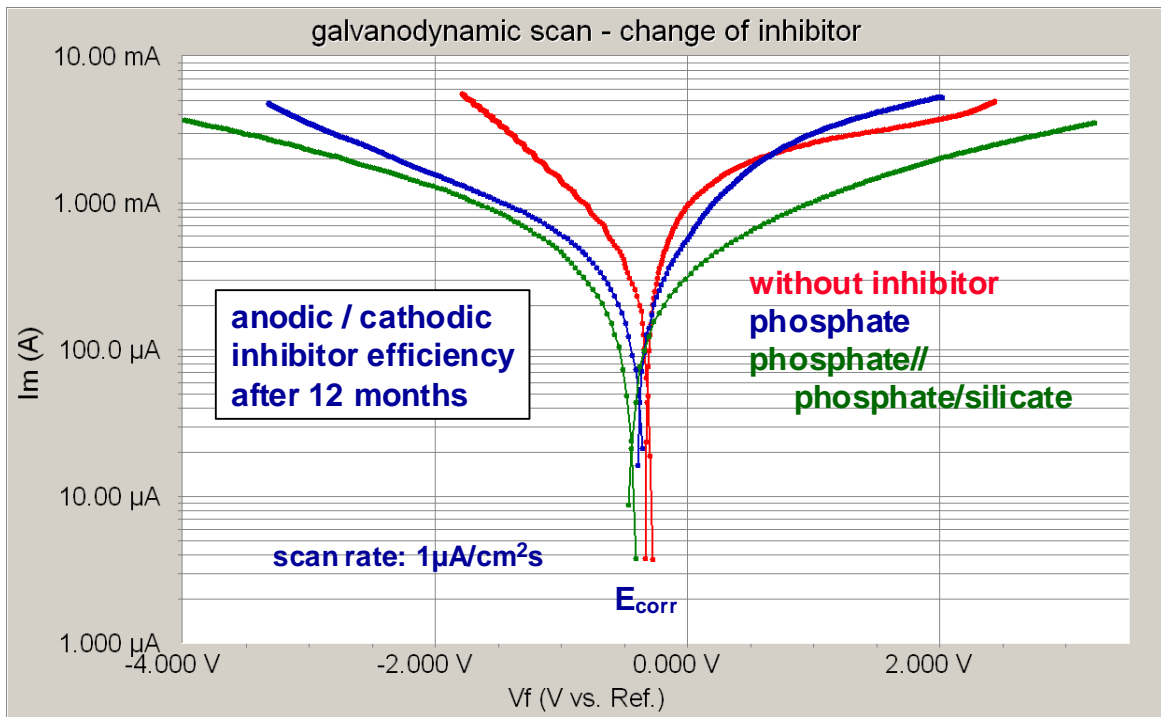


Figure 11: Effect of changing the inhibitor

To get a better overview and assessment of the surface layer characteristics due to corrosion protection, a distinct evaluation of all polarisation measurements over the whole three years operation time is obtained by calculating the polarisation resistance (figure 12). High values of the polarisation resistance correspond with good corrosion protection features.

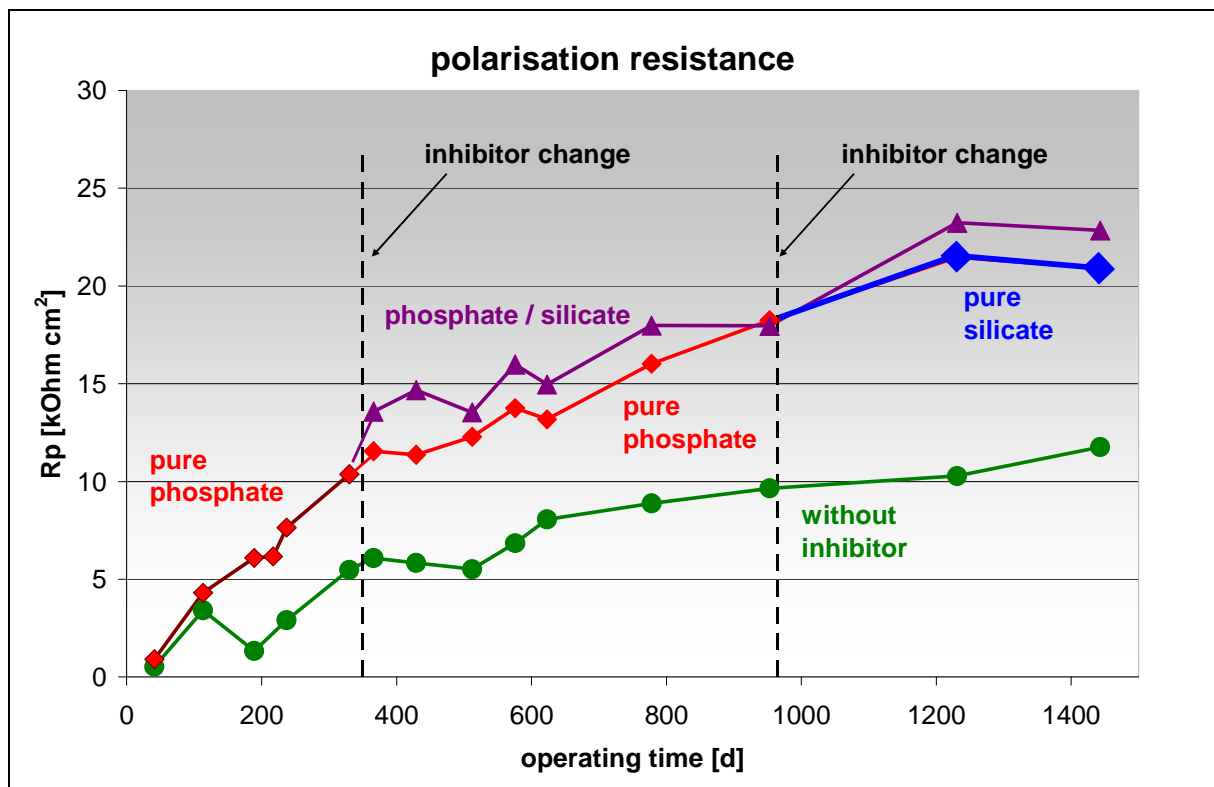


Figure 12: Polarisation resistance

The reciprocal slopes of the current potential curves near the free corrosion potential deliver the polarisation resistances. The polarisation resistances of the double equipment of the three electrodes array (counter and working electrodes at left and right side of the reference electrode) were averaged. Also the anodic and cathodic polarisation resistances were averaged to get a combined value for estimating the corrosion protection capability of a surface layer or to get a value for the efficiency of an inhibitor.

It is clearly visible that both inhibitors tested are effective inhibitors. The polarisation resistances of the inhibited test rigs samples are significantly higher than the ones of the uninhibited.

After changing the inhibitor composition in one test rig from the pure phosphate inhibitor to the combined phosphate/silicate inhibitor after 350 days the polarisation resistance in the system with the changed inhibitor became even higher. The efficiency of this inhibitor obviously is bigger.

After 950 days a second change was done. In the test rig in which remained before the pure phosphate inhibitor now a pure carbonate-activated silicate inhibitor was dosed. The efficiency of the pure carbonate-activated silicate inhibitor does not reach the efficiency of the combined phosphate/silicate inhibitor but the efficiency is in a comparable range not less to the phosphate inhibitor.

4 References

- [1] DVGW Arbeitsblatt W 215: Zentrale Dosierung von Inhibitoren
Teil 1: Phosphate
Teil 2: Silikatmischungen
- [2] Becker, A.: Möglichkeiten der Reduzierung von Rostwasserproblemen durch den zentralen Einsatz von Inhibitoren. Berichte aus dem Rheinisch-Westfälischen Institut für Wasserforschung gemeinnützige GmbH, Band 30, 1999
- [3] Hater, W.; Wagner, I.; Schmidt, P.: Experiences with application of inhibitors to reduce heavy metal uptake of drinking water. CEOCOR 6th International Congress, Giardini Naxos, 2003
- [4] Liste der Aufbereitungsstoffe und Desinfektionsverfahren gemäß § 11 Trinkwasserverordnung 2001. Stand Dezember 2011
- [5] Hater, W.: Zentraler Einsatz von Silikat-Mischungen als Korrosionsinhibitoren – das neue DVGW-Arbeitsblatt W 215-2. bbr 61(4), 2010, 60-65
- [6] Becker, A.; Ruhrberg, U.; Jentsch, T.; Kruse, C.-L.: Potenziale elektrochemischer Messverfahren für Korrosionsuntersuchungen. Berichte aus dem Rheinisch-Westfälischen Institut für Wasserforschung gemeinnützige GmbH, Band 48 (2009), 53-67