The Persistence of Inhibition of Copper Corrosion in Tap Water

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ABSTRACT

A method is presented to test the persistence of inhibition of corrosion of copper in previously inhibited tap water. Cyclic voltammetry (CV) sweeps on copper were carried out in tap water both in the presence and in the absence of inhibitor to examine the state of passivity and of breakdown leading to localised corrosion of the metal in tap water in order to investigate the persistence of inhibitor. The results show that after *prior* inhibition and re-immersion in inhibitor-free tap water, inhibition is still observed and persists through several further potential cycles. These novel observations describe the persistence of the inhibitor on the surface after the supply of the inhibitor has been removed.

1. Introduction

Copper is used as plumbing material for domestic water distribution systems and has been in use for several decades. Corrosion of copper used for potable water is a major and ongoing problem in many countries [1–6]. Localised, or pitting corrosion is recognised as one of the major problems with copper tubing failure in tap water [5,7]. It occurs in certain areas where the attack penetrates the pipe wall, causing water leakage through pinhole.

Corrosion inhibitors are widely used to minimise copper corrosion in tap water; to prevent plumbing pinhole generation and water leakage [2–4,8–30]. When added in small concentrations, inhibitors can effectively inhibit the corrosion reaction of the metal with the environment. Both inorganic inhibitors, such as phosphate inhibitors [3,4,8,9,12] and organic compounds such as azoles [11,13,15–29], amines [30] and amino acids [31,32] have been used as copper corrosion inhibitors but with organic compounds in greater number. Benzotriazole (BTA) is one of the most extensively used and effective inhibitors against copper corrosion [15–29].

Corrosion inhibitors can be applied continuously or in batches to maintain effective corrosion prevention [33,34]. We define persistence of the inhibitor as the ability of the inhibitor to resist detachment from the metal surface it protects when the source of the inhibitor is removed. Understanding and quantifying

persistence of the inhibitor is necessary for the batch treatment to aid determination of the frequency and amount of inhibitor involved.

A variety of techniques have been used for studies on film persistence tests. Esteban et al. employed the impinging jet system to evaluate inhibitor film persistency under high-speed fluid flow [35]. Tan et al. used electrochemical noise (EN) and electrochemical impedance spectroscopy (EIS) to monitor continuously the film performance and evaluate the inhibitor film persistency [33,36,37]. Heeg and Klenerman [38] studied the persistence of inhibitor films under multiphase flow conditions using a jet-cylinder electrochemical cell. Marco et al. [34] assessed the polarisation resistance in the long-term monitoring of corrosion rates for filmed electrodes in inhibitor-free electrolyte to assess the persistence of a broad range of batch treatment oil-field corrosion inhibitors. Ramachandran et al. [39,40] tested the film persistency of corrosion inhibitors using the wheel bomb apparatus. Although there is published research on inhibition persistence, limited work has been extended to the investigation of inhibition persistence for copper corrosion in tap water.

This work presents a new method to test the persistence of inhibitor for copper corrosion in tap water using cyclic voltammetry. Work in this paper has been carried out in tap water derived locally from the Cambridge water supply. Multi-cycle cyclic voltammetry tests have been carried out to study the localised corrosion of copper in tap water before and after inhibitor treatment and the persistence of inhibition effect on retarding the corrosion process. Persistence of inhibition of copper in tap water after previously being inhibited in the presence of a commercial

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inhibitor – Fernox® Alphi 11 and its main components: benzo-triazole (BTA) and triethanolamine (TEA) are presented.

2. Experimental Method

2.1. Materials

A three-electrode cell of volume 160 ml containing tap water (Cambridge tap water) was used in uninhibited form or in previously inhibited form containing 25% (by volume) Fernox®. The separate inhibitors were also examined: 4.7 mM benzotriazole (BTA), 30 mM triethanolamine (TEA) and a combination of 4.7 mM BTA and 30 mM TEA. The concentrations of BTA and TEA correspond to those present in 25% Fernox®. BTA and TEA were from SIGMA-ALDRICH. A Ø6.35 mm Cu rod (ADVENT, Oxford, UK, purity 99.99+%) mounted into epoxy resin with only the circular end surface exposed. The end surface was finished to 2400 (or 2500) grit with silicon carbide paper. This formed the working electrode (WE). The Cu electrode was left in air for 1 hour before testing. A Ag/AgCl electrode equilibrated with tap water, or a saturated calomel electrode (SCE) was used as the reference electrode (RE). A graphite rod formed the counter electrode. Analysis data of Cambridge tap water and components of Fernox® Alphi 11 are shown in Table 1. Note that Cambridge tap water is regarded as hard. [41]

2.2. Calibration for the Ag/AgCl reference electrode

Home-made Ag/AgCl electrodes or a saturated calomel electrode (SCE) were used as reference electrodes for cyclic voltammetry. The home-made Ag/AgCl electrode was made from a sheet of silver (40 mm × 40 mm) crimped to a piece of silver wire (Φ1 mm) and anodized in 1 M HCl solution for 10 min to produce a thick film of AgCl. A Solartron 1286 electrochemical interface was used to control the polarising process. For Fernox®-inhibited solutions, the reference potential of the Ag/AgCl electrode was affected by the presence of Fernox®. The potential of the Ag/AgCl reference electrode was calibrated against a saturated calomel electrode (SCE) in both inhibitor-free tap water and inhibitor-containing tap water (25 vol% Fernox®). The value of $E_{Ag/AgCl}$ in inhibitor-free tap water was +160 mV(SCE), and in Fernox®-containing tap water was +54 mV(SCE). Both were calibrated regularly. The potentials in this paper are presented against the SCE scale.

None of the data presented below have been corrected for the ohmic potential drop in the electrolyte. For the range of current densities covered by the inhibited surface, the ohmic potential drop is negligible. Using the formula of Newman [42] for the current flow to a disc electrode where the Luggin probe is infinitely distant, we calculate for a conductivity of 652 μS cm^{-1} (see Table 1)

that the resistance is 1208 Ω, or 383 Ω cm^2. The current densities relevant to the inhibited surface are all <7 μA cm^{-2}, giving a maximum ohmic drop of 2.7 mV, which is negligible. (The IR drop is nevertheless important for quantification the pitting regions where the current densities are much higher: analysis of the pitting current densities is however not the subject of this paper.)

2.3. Persistence of inhibition

The persistence of inhibition was examined using cyclic voltammetry as follows.

First, CV of Cu was carried out in tap water. The self-same electrode surface was then reground (to the same finish, and also left for 1 hour) and CV was carried out in Fernox®-inhibited, BTA, or TEA, or the mixture-inhibited (BTA + TEA) tap water. Two consecutive sweeps were carried out with the potential range of −0.8 V(SCE) to +0.4 V(SCE) at a sweep rate of 1 mV s^{-1}. This sample was then removed from the inhibited solution, washed thoroughly with twice-distilled water (but without further surface preparation), and immersed once again into *inhibitor-free* tap water for further repetitive CV measurements. These last measurements were thus made in inhibitor-free tap water, but with a surface still carrying any residual inhibition film from the inhibited solutions after washing. Cyclic voltammograms of Cu in tap water without inhibitor, and *after* the experiments with inhibitor are compared, both in uninhibited tap water. For these, the potential was swept linearly from −0.8 V(SCE) to +0.4 V(SCE) at a sweep rate of 1 mV s^{-1} in tap water and in tap water after previous inhibition. All these tests were carried out thermostatically controlled at 25 ± 0.1 °C in stirred solutions without deaeration. After two sweep cycles in previously inhibited tap water, the potential range was narrowed down according to the passivation region obtained. Multiple sweep cycles were carried out under thermostatic control, generally at 25 ± 1 °C, but with one experiment at 22 ± 2 °C. All were done without stirring.

3. Results

3.1. Persistence tests in tap water after previous inhibition in Fernox®-inhibited tap water

Fig. 1 presents the cyclic voltammetry of copper in uninhibited tap water and in inhibitor-free tap water after polarisation in Fernox®-inhibited tap water. It shows that the corrosion potential for the positive sweep for the surface which had previously been in inhibited tap water is very close to that which had not previously
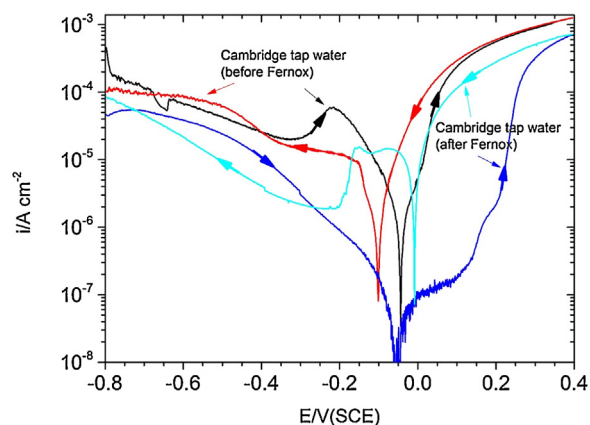
Table 1
Analysis data of Cambridge tap water and Fernox® Alphi 11 (data supplied by Mitsubishi Electric, UK; *: measured by the authors in the Cambridge laboratory) [41].

Cambridge tap water mg L^{-1}		Fernox® Alphi 11 mg kg^{-1}	
K$^+$	0.3	Cl$^-$	20
Mg^{2+}	2.4	SO$_4^{2-}$	<2
Ca^{2+}	121.0	triethanolamine	4300
Cl$^-$	26.5	benzotriazole	540
NO$_3^-$	0.1	PO$_3$	<2
PO$_4^{3-}$	39.4	P$_{total}$	<10
SO$_4^{2-}$	3.0	propylene glycol	99 wt%
Alkalinity	206		
pH	7.56*	pH	7.8
Conductivity/μS cm^{-1}	652*	Conductivity/μS cm^{-1}	33

Fig. 1. Cyclic polarisation curves for copper in inhibitor-free tap water without prior inhibition, and in inhibitor-free tap water after polarisation in 25% Fernox® inhibited tap water at 25 ± 0.1 °C.