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Investigation of pitting corrosion of a copper tube in a heating system

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ABSTRACT

Electrochemical tests, as well as surface and chemical analyses were used to examine the mechanism of pitting failure of a copper tube. Synthetic tap water simulating the hot water in a heating system and field-used heating water at 60 °C were used as electrolytes in these tests. The results showed that the presence of a Cu(I) oxide layer on the copper surface is essential for pitting corrosion of a copper tube in hot synthetic tap water. Moreover, the pitting corrosion of copper tubes is preferred in heating water containing higher concentrations of Fe species and under stagnant condition.

1. Introduction

Copper metal is used widely as a home plumbing material on account of its excellent corrosion resistance and ease of installation [1]. In Europe and North America, it accounts for more than 80% of all tubes installed in water services, amounting to more than 100 million meters of tubing. Copper corrosion is often considered to be an insignificant or at least a readily treatable problem in public water systems. The incidence of copper pipeline failure is relatively low despite the large quantities used in water services. However, pitting corrosion is a major problem with copper tubing accounting for approximately 60% of failures [2]. Considerable damage is caused by water leaking from corroded central heating systems.

Copper is assumed to be immune to corrosion by water itself. Copper corrosion in water is based on an interpretation of conventional potential-pH diagrams where the copper immunity range extends well above the hydrogen electrode potential. Thus the copper corrosion in aqueous solutions has been found to involve electron or charge-transfer between (1) copper dissolution and (2), (3) dissolved oxygen reduction reactions, which may be separated into partial or half-cell electrochemical reactions,

$$\text{Oxidation}: \mathrm{Cu} \rightarrow \mathrm{Cu}^{2+} + 2\mathrm{e}^- \tag{1}$$

and

$$\text{Reduction}: \mathrm{O}_2 + 4\mathrm{H}^+ + 4\mathrm{e}^- \rightarrow 2\mathrm{H}_2\mathrm{O} \tag{2}$$

$$\mathrm{O}_2 + 2\mathrm{H}_2\mathrm{O} + 4\mathrm{e}^- \rightarrow 4\mathrm{OH}^- \tag{3}$$

representing equivalent reduction reactions in (2) acid and (3) neutral or alkaline solutions, respectively.

Pitting corrosion of copper tubes can be classified into two types according to the morphology, corrosion products and water in which it occurs, as shown in Table 1 [1–3]. The electrochemical behavior of copper in alkaline solutions has been analyzed by many researchers over the past few decades [4,5]. However, there has been little success in gaining an

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Table 1
Comparison of the two types of pitting for copper tube.

	Type I pitting	Type II pitting
Pit shape	Deep and narrow	Narrower than type I
Scale morphology	Underlying Cu_2O with overlying malachite, calcite or other basic copper salts, occasionally CuCl underlies Cu_2O	Underlying Cu_2O with overlying bronchantite, some malachite
Water quality	Hard, cold, well waters between pH 7 and 7.8, high sulfate relative to chloride and bicarbonate, high CO_2	Hot waters, pH below 7.2, high sulfate relative to bicarbonate, occasional Mn deposits
Initiating factors	Stagnation early in pipe life, deposits within pipe including dirt of carbon films, high chloride residuals, water softeners, alum coagulation	Higher temperatures, high chlorine residuals, alum coagulation, particles

understanding of copper pitting corrosion. Moreover, the ability to assess, explain or mitigate the occasional problems that do occur is limited because pitting is unpredictable, especially in conditions forming deep pits. The rate, depth, surface size and density of pitting are variable, depending on uncertain migration of corrodents into and out of the pit. Thus, average corrosion rate are inadequate for pitting evaluations because even a very small loss can be concentrated in a few pits, with those of maximum depth penetrating the wall thickness to produce failure by leakage [6].

Although many studies have attempted to reproduce, quantify and elucidate the mechanisms of practical copper pitting failures, the current theories are inconsistent with many aspects of the real performance. In this study, electrochemical tests, surface and chemical analyses were carried out to examine the cause of pitting failure and evaluate the effects of the operational conditions on copper corrosion.

2. Materials and methods

2.1. Analyses of field-used copper tubes with pitting failure

2.1.1. Visual examination

Two types of copper tubes (summarized in Table 2) used in central heating system were sectioned to observe the internal surfaces. Two different specimens with pitting failure were examined by a visual inspection and scanning electron microscopy (SEM). Deposits of green corrosion products on the internal side of the copper tubes in Fig. 1 were removed carefully by scrubbing to reveal the underlying metal. A reddish-brown film and pits penetrating into the tube wall were observed beneath the green scale.

2.1.2. Chemical analysis of scale and corrosion products on the field-used copper tubes

Powder X-ray diffraction (XRD) and bulk XRD techniques were performed using Bruker D8 and Rigaku 12 kW diffractometer equipped with a Cu Kα source to analyze the scrubbed green-colored deposit and corrosion products on the field-used copper surfaces, respectively.

2.1.3. Chemical analyses of field-used heating water for two areas, A and B

The impurity (Cu, Fe, Ca, Mg) and corrosion inhibitor (PO_4, index for phosphates) concentration of the heating water in two areas, A and B, were determined by atomic absorption spectroscopy (AAS). The conductivity and pH of the heating water were also measured.

2.2. Electrochemical tests

2.2.1. Materials and preparation

Specimens of cylindrical pure copper tubing (>99.9%) with a diameter and thickness of 12.5 and 1.3 mm, respectively, were used for the electrochemical tests. All specimens were polished mechanically with 600-grit SiC polishing paper and cleaned with ethanol in an ultrasonic vibrator for 10 min. As shown in Table 3, synthetic tap water was used as the corrosion medium to simulate heating water. The water was prepared from distilled water and reagent grade HCl, H_2SO_4, $MgSO_4 \cdot 7H_2O$

Table 2
Field-used copper tubes for two areas, A and B.

	A	B
Material	Phosphorus deoxidized copper	
Size	15.88(d) × 1.02(t) mm	19.05(d) × 1.07(t) mm
Service period	2.5 years	3 years