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Impact of chlorinated disinfection on copper corrosion in hot water systems

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In France, hot water quality control inside buildings is occasionally ensured by disinfection treatments using temperature increases or addition of sodium hypochlorite (between 0.5 ppm and 1 ppm residual free chlorine). This disinfectant is a strong oxidiser and it could interact with metallic pipes usually used in hot water systems. This work deals with the study of the impact of these treatments on the durability of copper pipes. The objective of this work was to investigate the influence of sodium hypochlorite concentration and temperature on the copper corrosion mechanism. Copper samples were tested under dynamic and static conditions of ageing with sodium hypochlorite solutions ranging from 0 to 100 ppm with temperature at 50 °C and 70 °C. The efficiency of a corrosion inhibitor was investigated in dynamic conditions. Visual observations and analytical analyses of the internal surface of samples was studied at different ageing duration. Corrosion products were characterised by X-ray diffraction and Raman spectroscopy. Temperature and disinfectant were found to considerably affect the copper corrosion mechanism.

Surprisingly, the corrosiveness of the solution was higher at lower temperatures. The temperature influences the nature of corrosion products. The protection efficiency is then strongly depend on the nature of the corrosion products formed at the surface of copper samples exposed to the aggressive solutions containing different concentration of disinfectant.

1. Introduction

Generally, temperature of hot water distribution systems is often maintained at 50 °C [1]; however, poor network seizing can create favourable conditions for microbiological growth (for example: Legionella) [2]. In order to prevent the development of bacteria, the use of disinfection treatments is currently applied in hot water systems.

They represent the most efficient treatment to control microbiological growth. Several products can be used to ensure disinfection. Sodium hypochlorite (NaClO), between 0.5 ppm and 1 ppm residual free chlorine (1 ppm equals 1 mg L^{-1}), is the most used for treating hot water distribution systems [3,4]. It must be noted that shock chlorination treatments are also used with a concentration up to 100 ppm without any pH control. The concentration of the disinfectant decreases rapidly [5,6] after the shock treatment however materials are exposed during a short period to highly aggressive media that could affect their durability.

Sodium hypochlorite chemistry is complex and chlorine undergoes many chemical reactions in aqueous phase. The chemistry of sodium hypochlorite solutions is highly dependent on the pH and the temperature of the solution, *i.e.* the species present at low pH or temperature are different from those present at high pH or temperature. Sodium hypochlorite solutions are well studied at ambient temperature [6–15]. Chlorinated water is most accurately described in terms of the pH-dependent concentration profiles of three species: Cl_2, HClO and ClO^-. These species are connected through the following equilibrium reactions:

$$HClO + H_2O \Leftrightarrow ClO^- + H_3O^+ \quad (1)$$

$$Cl_2 + 2H_2O \Leftrightarrow HClO + H_3O^+ + Cl^- \quad (2)$$

Alkaline systems with a pH greater than 9 are characterised by a high concentration of ClO^-. Upon acidification, the concentration of HClO increases, reaching a maximum at a pH close to 4. Upon continued acidification, and at pH values below 4, HClO concentration decrease is followed by an increase in the concentration of Cl_2.

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Table 1
Studies about corrosion of copper pipes.

Condition	Concentration ($mg\,L^{-1}$)	Temperature (°C)	pH	Ageing time (h)	Results	Ref.
Static	6 (NaClO)	Ambient	5 and 8	24	• Disinfectant increased corrosion rate at pH 5	[14]
Dynamic	34 (Cl^-)	Ambient	7.6	4 (accelerated ageing)	• The presence of chloride ions decreased corrosion rate of aged pipes	[53]
Static	0.7 and 1.5 (NaClO)	4, 20, 24 and 60	7 and 9.5	4320 (6 months)	• Corrosion rate is 5 times higher at pH 7 • Corrosion rate is increased at 60 °C • Disinfectant did not increase corrosion rate at pH 7 • Disinfectant increased corrosion rate at pH 9.5	[15]
Dynamic	Not reported (Cl^-)	18	9.3	24 (accelerated ageing)	• Chloride ion addition decreased corrosion rate of aged pipes	[42]
Dynamic	1 (NaClO)	Ambient	7	12960 (18 months)	• Disinfectant addition had not influence the time required to reach a steady state of corrosion • Measured corrosion rate: 0.3 mm/year	[40]
Dynamic	0	Ambient	7; 7.5; 8; 9	8640 (12 months)	• Corrosion inhibitors decreased copper corrosion rate	[41]

At ambient temperature and drinking water pH values (commonly between 6.5 and 8.5) the chemical species present in hypochlorite solutions are HClO and ClO^-. A recent study shows that, at constant pH value, when temperature increases the HClO content decreases [5]. Hypochlorous acid (HClO) is considered to be a much more potent oxidiser than hypochlorite anion (ClO^-) [6,7]. So, sodium hypochlorite solutions could be less corrosive at 70 °C than at 50 °C.

Many studies showed that sodium hypochlorite was able to affect the lifetime of polymer and metallic pipes [16–28]. Corrosion inhibitors, mainly composed of phosphates and silicates, were used to prevent the deterioration of metallic pipes. These corrosion inhibitors were usually used for the long time protection of galvanised steel pipes [29,30] or copper pipes [11,12,31]. Edwards suggested that these inhibitors reduced the copper solubility favouring the formation of a cupric phosphate layer [11]. However, the mechanism of these inhibitors onto copper was not clearly understood.

Copper pipes usually corroded according to a two steps pathway [32–38]: firstly metallic copper (Cu^0) oxides to Cu^+ forming cuprite (Cu_2O). Secondly, copper oxides from Cu^+ to Cu^{2+} forming mainly tenorite (CuO), malachite ($CuCO_3Cu(OH)_2$) or copper sulphates.

Localised or pitting corrosion is the major cause of water pipe failures [39] at pH values of hot water distribution systems (between 6.5 and 8.5). Chlorine is not essential for the initiation of pitting corrosion, but it is a stronger oxidant than oxygen. Fujii and Suzuki [40,41] have found a relationship between the free chlorine concentration and the copper pitting susceptibility.

Other authors have studied the influence of temperature and disinfectant concentration on copper pipe corrosion under dynamic or static conditions [16,17,42–44]. Atlas et al. [16] and Boulay et al. [17] studied the influence of the addition of sodium hypochlorite (between 0.7 and 6 ppm) on copper corrosion under stagnant conditions. Both studies showed that sodium hypochlorite can accelerate copper corrosion rate. However, the influence of sodium hypochlorite strongly depends on the solution pH. Boulay et al. [17] studied the influence of temperature on copper corrosion. Four different temperatures were investigated: 4 °C, 20 °C, 24 °C and 60 °C. They did not find significant differences for the lower temperatures up to 24 °C. But, they found a significant increase of the copper corrosion rate at 60 °C. Dissolution of copper is normally a thermally activated process and the increase of temperature induces an increase of the dissolution kinetic of copper. However, the stability of copper oxides also depends on the temperature variation, so the results obtained by Boulay would suggest modifications on the nature of the copper oxides. Treweek et al. [42] compared the efficiency of sodium hypochlorite compared with another disinfectant (monochloramine) under dynamic conditions at ambient temperature. They concluded that copper corrosion did not seem to be influenced by the nature of disinfectant. MacQuarrie et al. [43] studied the efficiency of corrosion inhibitors (composed of phosphates and silicates) under dynamic conditions at ambient temperature. They found that corrosion rates were between 2 and 5 times lower on copper pipes treated with corrosion inhibitors. Anyway, no explanation was drawn to explain the decrease of the copper reactivity in presence of the inhibitors.

In resume, literature agrees that sodium hypochlorite addition can increase copper corrosion rate. A temperature increase also seems to accelerate copper corrosion. However, synergies between temperature increase and sodium hypochlorite addition was not thoroughly investigated. It was reported that the use of corrosion inhibitors based on phosphate or silicate compounds are effective in the reduction of the material degradation. But the efficiency of corrosion inhibitors was not studied at temperatures of hot water distribution systems with the addition of disinfectant.

Table 1 summarises some works dealing on the copper pipe durability. In this table, chlorides had also been considered because they can be produced during then copper/disinfectant corrosion reactions, or they can be added with sodium hypochlorite solutions.

The aim of this study is to evaluate the influence of the addition of sodium hypochlorite and of a commercial corrosion inhibitor on the corrosion mechanism of copper pipe at the temperature range of hot water distribution systems (50 °C < T < 70 °C).

2. Materials and methods

2.1. Material and sample preparation

Cylindrical samples were cut out from commercial hot water copper pipes with 50 mm internal diameter. Pipes conformed to French (NF) standards. The length of the cylinders was varied according to the ageing device from 10 to 20 cm.