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Impact of chlorinated disinfection on copper corrosion in hot water systems

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Abstract:

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 oxidizer 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 characterized 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.

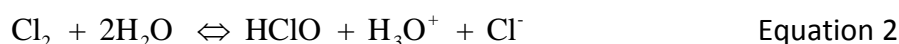
Keywords: Copper, Corrosion, Sodium hypochlorite, Hot water

1.0 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: Cl₂, HClO and ClO⁻. These species are connected through the following equilibrium reactions:



Alkaline systems with a pH greater than 9 are characterized 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 Cl₂.

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 oxidizer 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 galvanized steel pipes [29, 30] or copper pipes [11, 12, 31]. Edwards suggested that these inhibitors reduced the copper solubility favoring 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 (Cu⁰) oxides to Cu⁺ forming cuprite (Cu₂O). Secondly, copper oxides from Cu⁺ to Cu²⁺ forming mainly tenorite (CuO), malachite (CuCO₃Cu(OH)₂) or copper sulfates.

Localized 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 summarizes 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 ($50^{\circ}\text{C} < T < 70^{\circ}\text{C}$).

2.0 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.

The procedure used for the cleaning of copper samples before the ageing period in contact with a chlorinated solution was as follows:

- a. Cleaning each sample with tap water to remove manufacturing residue.
- b. Rinsing the samples with distilled water.
- c. Rinsing the samples with ethanol and air dry.

Experiments were realized under static and dynamic conditions. Experiments realized under dynamic conditions were carried out using a one scale pilot. The pilot reproduces a hot water distribution system at a unit scale. The pilot was designed in order to obtain different configurations of samples, in horizontal and longitudinal positions according to the solution flow.

2.1.1 Static tests

Samples used for static tests had a length of 10 cm. Samples were filled with the solution using a semi-closed system as presented in figure 1. Samples were kept in temperature-calibrated ovens (Mettert UFE 500 equipped with a fan) at 70°C. This temperature is the highest value that could be applied during the disinfection treatment in hot water systems. So we have tested the highest aggressive conditions in terms of temperature and disinfectant concentration in order to evaluate the impact on the copper degradation.

Sodium hypochlorite solutions were prepared with tap water of Nantes at 0 and 100 ppm free chlorine contents. The tap water contained approximately 0.05 ppm of residual free chlorine. Table 2 presents the concentration of the main chemical species detected in the Nantes tap water. Chlorine is unstable in water; therefore, all solutions were prepared and renewed daily except during the weekends. When the solution was in contact with samples, chlorine was rapidly consumed. In fact, after 5 hours, chlorine levels were lower than 20% of the initial level. The evolution of the chlorine content was also investigated in solutions entrapped inside glass bottles and the consumption rates depend on the material, solution

composition, pH and temperature [6]. Chlorine consumption seems to be mainly due to chlorine / copper reactions occurring at high temperature (70°C) as reported by Rushing [45]. Free chlorine concentration was measured according to an adaptation of the standard Method 4500-Cl G. A PhotoFlex WVR portable ions analyser was used.

The solution pH was not adjusted after the addition of sodium hypochlorite. The pH was measured using a multi-parameter analyser Consort C862 with platinum probe. The pH of the 100 ppm solution was measured at 9.3 ± 0.2 while the pH of the 0 ppm solution was measured at 8 ± 0.2 . Even though the pH was not adjusted, HClO and Cl₂ species were not present under static test conditions. Therefore, hypochlorous anion (ClO⁻) was the main oxidizing chlorine specie on experiments realised under static conditions [46].

2.2.2 Dynamic tests

Dynamic tests were conducted using a 1 scale pilot-plant. The objective is to reproduce the real conditions of disinfectant treatments on hot water systems. The pilot-plant design, presented in figure 2 consisted of three parallel flow lines sets that operated simultaneously. The flow lines were pipe loops. One loop was a control loop where temperature was regulated at 50°C and chlorine concentration was regulated at 1 ppm. This reference loop corresponds to the conventional conditions used in real hot water treatments. Each pipe loop was 11 m length and was mainly composed of cPVC pipe. Several 23 cm copper sections of 50 mm inner diameter were inserted vertically and horizontally (figure 2). Copper sections were joined together with EPDM repair clamps (Flex Seal Plus® SC65).

Nantes tap water was used as the source water for the pipe loops. Water was recirculated using a centrifugal pump AES-MAX. Water pressure was regulated to provide constant pressure in the pipe loops. In order to create a constant flow velocity through the copper samples similar to that used in household plumbing, manually operated valves were employed. Water temperature was controlled using a 3000 W heater (CETAL 67501). The pH of the water was maintained at 7.2 ± 0.2 using a pH controller DULCOMETER® D1C coupled to a ProMinent® WA-PH1 probe and a metering pump ProMinent® CONCEPT_{PLUS}. Chlorine concentration was maintained constant. Chlorine was added continuously to the pipe loop using a metering pump ProMinent® CONCEPT_{PLUS} coupled to a DULCOTEST® CLE probe. The solution contained inside the pipe loop was constantly renewed using an electrically operated valve coupled with a flow-meter and a discharge valve. This system ensure a

retention time of 10 hours. In one test loop a metering pump allowed the injection of H3111 solution (Veolia commercial product) which is a corrosion inhibitor based on polyphosphates and silicates and conventionally used in hot water systems.

Three factors were tested in dynamic conditions: temperature, chlorine concentration and the addition of the corrosion inhibitor.

Conditions of dynamic tests are summarized in table 3.

2.2. Characterisation techniques

μ -XRF analysis were performed on the as received copper samples using a Bruker M4 Tornado with a Rhodium filament excited at 30kV and 200 μ A. Gaussian deconvolution was used to extract the composition of the samples.

After ageing, copper samples were kept into a desiccator prior to visual analyses. Pipes were then cut axially. The internal surface of each pipe section was photographed with a digital camera.

Corrosion scale of some samples were subsequently analysed with a Scanning electron microscopy (SEM) Philips Quanta 200 ESEM/FEG coupled to a EDAX GENESIS detector to perform Energy Dispersive Spectrometry (EDS) analyses.

Finally, corrosion products identification was carried out by performing X-Ray diffraction (XRD) and μ -Raman spectroscopy. X-ray diffraction measurements were carried out with a Bruker AXS D8 Advance diffractometer using $\text{CuK}\alpha$ radiation (0.15406 nm) in the $\theta/2\theta$ configuration. Micro-Raman spectra were recorded using a Jobin Yvon High Resolution Raman spectrometer (LabRAM HR). Excitation was provided by a He-Ne laser (632.33 nm) through a confocal Olympus microscope. Raman bands were identified through previous works [47-53].

3. Results and discussion

Static tests in unstirred chlorinated hot water were realised in order to determine the ageing indicators associated to the copper degradation. Therefore, dynamic tests were carried out in order to determine how sodium hypochlorite concentration and temperature influence

the copper corrosion. The effectiveness of a corrosion inhibitor conventionally used in hot water pipe devices was also tested under dynamic conditions.

3.1. Static tests

Copper samples filled with solutions at 0 or 100 ppm sodium hypochlorite concentrations were aged during 45 days at 70°C. The solutions with sodium hypochlorite were periodically renewed in order to limit the impact of the disinfectant consumption during the degradation of the material. Table 4 summarizes the investigations realised under static conditions.

3.1.1 Visual observations

Uniform corrosion was observed in all static tests performed at 70°C. Water pH was higher than 8, so uniform corrosion was the expected corrosion mode as reported in the literature [54].

The aspect of corrosion products was similar for samples immersed in solution with 0 and 100 ppm. Corrosion products were between dark brown and black. Corrosion products became darker with ageing period. Corrosion products of samples aged at 100 ppm were slightly darker than corrosion products of samples aged at 0 ppm. In a first approach, it can be thought that the addition of disinfectant (electron acceptor) increases corrosion kinetics [54] which implied that corrosion layer formed at 100 ppm was thicker than the corrosion layer formed at 0 ppm.

3.1.2 Corrosion product identification

The X-ray patterns of samples aged during 0, 8 and 45 days are shown in table 5. A copper sulfide was detected in the copper tube. XRF analysis realized on the cross section of the copper tube effectively revealed a slight enrichment of sulfur at the pipe surface. Close to the surface, the content was approximately at 0.15 wt% whereas in the bulk, the content is quite constant at 0.02 wt%. This compound is probably due to the presence of impurities or inclusions.

X-ray patterns of samples aged at 0 ppm did not show peaks corresponding to copper corrosion products, whatever the immersion period is concerned. In these conditions of pH and temperature, the reactivity of copper pipe is very low so we could suppose that a very thin, adherent and protective cuprous oxide film appears on the surface of the samples.

Diffraction peaks associated with cuprite Cu_2O appeared after 45 days of ageing on samples aged at 100 ppm sodium hypochlorite solution. 45 days of immersion was insufficient to form a corrosion product film containing a mixed composition of cuprite/tenorite on copper samples as it was previously observed by Xiao et al. [32]. Feng et al [55] studied the composition of the copper corrosion product film during extended immersion in simulated tap water at 30°C and $\text{pH} = 7.6$. The film was mainly composed of Cu_2O , and small amounts of CuO and $\text{Cu}(\text{OH})_2$ were detected at the surface of the corrosion products.

Figure 3 shows the Raman spectra of samples exposed during 45 days with solutions at 0 and 100 ppm. Cuprite Cu_2O was the main corrosion product for both conditions. During the exposure period in solution without sodium hypochlorite, a cuprous oxide film gradually appears whereas the presence of hypochlorite ions seems to accelerate the copper degradation favouring a thicker corrosion product film. Presence of CuO was also detected on 100 ppm aged samples, but the tenorite amount was very low explaining why it was not detected on XRD diagrams. Tenorite indicates a more advanced corrosion state compared with samples exposed to reference tap water [32-37, 55]. The presence of the disinfectant considerably amplifies the degradation through additional cathodic reactions that normally accelerate the pH alkalisation at the surface vicinity. The pH increase favors the stability of the copper oxide species, and specially the transformation of cuprite into tenorite [56-59].

In conclusion, the addition of sodium hypochlorite at 100 ppm did not affect the corrosion mode of copper samples in static conditions. A uniform degradation of the copper samples occurred. Fujii and Suzuki have realized the ageing of copper samples in tap water with 100 ppm of sodium hypochlorite at 60°C under dynamic conditions. They suggested that the presence of residual chlorine levels at around 2-3 ppm in tap water was able to provoke a copper pitting in hot water systems [40,41]. Degradation of copper samples in hot water systems was mainly influenced by the concentration of residual chlorine, the pH, the temperature and the flow rate [41]. Suzuki revealed that the presence of cuprous oxide corrosion product film combined with a solution containing residual chlorine were the main factors that are necessary for the pitting corrosion of copper pipe. But this localized

corrosion mechanism appeared only after an incubation time depending on the chemical stability of the corrosion products [40,41].

Corrosion products were mainly copper oxides (cuprite and tenorite) as it was expected at 70°C according with the thermodynamic calculations of Adeloju [60]. Finally, the corrosion kinetics seems to be accelerated in the 100 ppm sodium hypochlorite solution. So, as predicted by Edwards [54], the addition of disinfectant increases the corrosion kinetics of copper.

3.2. Dynamic tests

The dynamic tests were the most realistic tests for the application of hot water systems. pH was continuously regulated, as well as temperature and concentration of the sodium hypochlorite. The influence of three parameters was tested under dynamic conditions:

- a. Temperature, at 50°C and 70°C.
- b. Sodium hypochlorite concentration, at 1 ppm and 25 ppm.
- c. The addition of a commercial corrosion inhibitor.

Copper samples were aged during 8 weeks in a 1 scale pilot. Table 3 summarizes the configurations that were investigated during this study. Reference samples were aged during 4 weeks in a system loop using the conventional parameters in conventional hot water systems (1 ppm, 50°C). The parameters used in the dynamic ageing tests are summarized in figure 4. Samples were horizontally and vertically tested. However, there were not significant differences between both configurations. Results presented below correspond to samples aged according to the vertical configuration. The degradation of the copper samples was mainly associated to the characterisation of the corrosion products during immersion. So copper samples were analysed at different immersion exposure times in order to follow the evolution of the nature of the corrosion products.

3.2.1 Visual observations

Table 6 shows the inner surface of samples aged vertically after different weeks and conditions as presented in the table.

Temperature seems to have an impact on copper corrosion with the same concentration of disinfectant. At 70°C the corrosion was uniform. The surfaces of the copper pipes were covered with brown corrosion products. At 50°C, the copper surface is also tarnished after 2 week of ageing, but by comparing with the surface exposed at higher temperature, it seems that the degradation is slightly different. After 4 weeks of ageing at 50°C, localized degradation is observed consisting on few circular pits. The surface of the copper pipes was covered with brown corrosion products and few shallow and broad pits were observed after 4 weeks. At the bottom of pits, green corrosion products were detected.

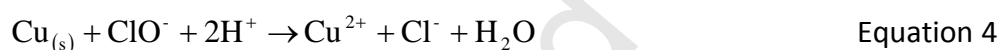
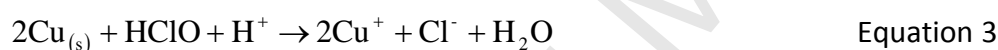
Sodium hypochlorite concentration also seems to influence the copper deterioration as it was previously suggested by Fujii [40]. Actually, samples aged with 25 ppm sodium hypochlorite concentrations at 50°C showed pitting corrosion after 4 weeks of ageing while samples aged with 1 ppm corroded uniformly. As suggested by Fujii and Suzuki, an incubation period is needed in presence of residual chlorine to detect pitting corrosion on copper pipe. In the case of Fujii study, it was observed the presence of pitting corrosion on copper pipe exposed at 60° in solution with residual concentration of chlorine at around 2-3 ppm after approximately 113 days [40]. According to Fujii considerations, the solution with 1 ppm of sodium hypochlorite at 50°C would normally lead to low residual chlorine content.

The addition of a commercial corrosion inhibitor seems to influence the nature of the corrosion products. The morphology, the amount and the color of the corrosion products formed with or without the corrosion inhibitor was significantly different. Moreover, at 50°C the addition of the corrosion inhibitor drastically delayed the apparition of pitting. Pitting appeared after 4 weeks without corrosion inhibitor but it appeared after 8 weeks with the corrosion inhibitor. Therefore, the addition of the corrosion inhibitor seems to protect the copper pipes in agreement with the studies of MacQuarrie et al. [43].

Literature underlined the fact that the pit formation could be favored by high temperatures [54]. Surprisingly, for 25 ppm sodium hypochlorite solutions, we observed pitting corrosion

at 50°C while no pits were detected at 70°C. Hypochlorous acid is considered to be a much more potent oxidizer than hypochlorite ion [7]. According to the concentration profiles of sodium hypochlorite [5,6], hypochlorous acid concentration was around 30% higher at 50°C than that at 70°C. Therefore, the solution was more corrosive at 50°C which could promote the pitting attack.

The mechanism leading to copper pitting in hot water distribution systems is poorly understood but, most of authors agree that chloride anions play an important role on pitting initiation [39, 40, 54]. Copper corrosion by sodium hypochlorite (equations 3 and 4) can indirectly influence the durability of copper structure and conductivity through the formation of copper chloride [61]. The pit initiation is linked to the formation of a porous layer of corrosion products [41]. In presence of chloride anions, corrosion products are composed of a mixture of copper oxides, copper hydroxychloride and copper hydroxide. Local increase of the chloride concentration due to the presence of defects in the corrosion product film leads to the pH decrease. These factors are known to favor the pitting corrosion [54].



3.2.2 SEM analysis

SEM observations and EDX analysis were used to observe the pit microstructure. Table 7 shows SEM pictures of broad pits observed on samples aged without corrosion inhibitor at 50°C and 25 ppm sodium hypochlorite concentration after 4 and 8 weeks of exposure. SEM micrograph reveals formation of porous structures. The EDX analysis of these porous structures reveals an elemental composition of mainly copper, oxygen and carbon. These structures have been previously addressed by Vargas et al. [34, 62] and Merkel et al. [63] and were identified as malachite ($\text{Cu}(\text{OH})_2 \cdot \text{CuCO}_3$).

Moreover, in agreement with Lytle et al. observations [39], chlorine was mainly absent from the center of the pits.

3.2.3 Identification of the nature of the corrosion products

Figure 5 shows the Raman spectrum of the copper samples exposed to the reference conditions (50°C and 1 ppm after 2 and 4 weeks of exposure). Only cuprite Cu_2O was detected on the surface of the corroded samples, whatever the period of ageing. In these conditions of pH and temperature, cuprite was the expected corrosion product, the amount of disinfectant was insufficient to increase the deterioration of the copper pipe. A uniform degradation of the copper pipe is then observed during the 4 weeks of exposure.

Table 8 gathers the Raman spectrum of the samples exposed to various conditions of temperature and disinfectant concentration compared to the reference condition (50°C and 70°C, with or without corrosion inhibitor). These parameters affect the nature of the corrosion products formed during the degradation of the copper pipe. The evolution of these products during the ageing period was investigated and the sequence of corrosion products is presented in the figure 6.

Formation of cuprite Cu_2O represents the first stage of deterioration of copper pipe in hot water distribution systems. According to Suzuki, without addition of sodium hypochlorite, a cuprous oxide layer is rapidly formed on the copper surface [41]. It was then reported that the presence of this corrosion products films leads to an ennoblement of the open circuit potential that reaches a limited value at around +60 mV/SCE.

Increase of temperature or disinfectant concentration seems to accelerate the degradation of copper pipe without modifications of the elemental mechanisms of degradation. Concerning samples aged without corrosion inhibitor and with a concentration of 25 ppm of disinfectant, it should be reported that the temperature influenced the nature of corrosion products. At 50°C, malachite ($\text{Cu}_2\text{CO}_3(\text{OH})_2$) was the main corrosion product after 8 weeks of ageing. At higher temperature 70°C, tenorite (copper oxide) was observed as the main corrosion product after 8 weeks of ageing. These results are in good agreement with the thermodynamic calculations evaluated by Adeloju [60]. Adeloju et al. predict that above 50°C, the formation of tenorite is favored over malachite formation. When temperature is increased up to 70°C, tenorite is the main product, and as it was reported by Feng et al. [55], this film of corrosion products was porous and more protective than the one composed

mainly of cuprite. The absence of malachite for samples aged at 70°C is directly linked to the solubility of CO₂ gas that is reduced in this range of temperature, preventing the formation of this corrosion product contrary to the samples aged at lower temperature (50°C).

An increase in the disinfectant concentration seems to accelerate the corrosion kinetics in agreement with results observed during the static tests. After 4 weeks of ageing, the main corrosion product detected on samples exposed to the reference electrolyte (50°C and 1 ppm of sodium hypochlorite) was the cuprite. Copper immersed in an oxygenated aqueous solution rapidly corrodes to form cuprite [54]. But, copper corrosion rate has been observed to be governed by the precipitation of Cu(II) solid phases like malachite or tenorite which appear from the transformation of cuprite [38]. Our samples exposed to a solution with 25 ppm of sodium hypochlorite showed the presence of Cu(II) corrosion products even, after 2 weeks of ageing. Under our test conditions, the predominant electron acceptors (i.e., oxidants for copper) were dissolved oxygen and disinfectant species. So, the increase of the corrosion kinetics can be explained by the fact that the test loops had more oxidant species available compared to the reference loop [54]. Similar results were observed by Suzuki et al. who concluded that hypochlorous acid accelerated the formation of the Cu₂O layer [41].

Raman spectrum had been recorded on the mounds of the pits (figure 7). The Raman spectrum of the pit (figure 7) displays one major band at ~970 cm⁻¹. This band may be attributed to a Cu(II) sulfate mineral (chalcantite). Several lower intensity peaks corresponding to the malachite were also found. These corrosion products are characteristic of hot water pitting (pitting II). In fact, literature describes hot water pits as relatively narrow, with an exterior scale layer invariably containing copper sulfates and some malachite [54]. Fujji had reported that different types of pitting could be experimentally reproduced in presence of chlorine depending on the water composition. When pH of water is between 6.5 to 7 with a bicarbonate-sulfate ratio between 0.4 to 1, the main corrosion product above pits was reported as Cu₄SO₄(OH)₆ that suggest the pitting II mechanism whereas when pH of water is superior to 7 with a bicarbonate-sulfate ratio between 1.7 to 2.8, the main corrosion product was malachite CuCO₃.Cu(OH)₂ suggesting the pitting I mechanism [40].

Nantes tap water have a bicarbonate-sulfate ratio higher than 1 ($\frac{[HCO_3^-]}{[SO_4^{2-}]} > 1$) at 25°C, so in presence of chlorine, we could expect to observe pitting corrosion involving mainly the formation of copper hydroxycarbonate.

On test samples, cuprite also appeared in the early stages of ageing. XRD was employed in order to get further information about the nature of the corrosion layer of samples aged with the corrosion inhibitor (figure 8). It is clear that the corrosion inhibitor influenced the nature of corrosion products.

At 70°C, chalcantite and atacamite only appeared in the presence of the corrosion inhibitor. But, in contrast with Edwards, who suggested that the inhibitor reduces copper solubility forming a cupric phosphate layer [11], neither copper phosphates nor copper silicates were observed. The inhibitor seems to modify the solution chemistry at the copper surface delaying the degradation mechanism previously observed in the absence of this commercial inhibitor.

4 Conclusions

In order to limit bacteria development in hot water distribution systems, disinfection treatments are used. In this study, multiple approaches were used to investigate the impact of disinfection treatments on copper pipe corrosion, but the most original approach comes from the development of a 1 scale pilot that permits to reproduce the real conditions of use of hot water systems. The pilot permits to reproduce the industrial treatments that are commonly applied for the disinfection treatments of hot water systems (thermal or chemical shocks) Our results suggest that the corrosion processes of copper pipes are significantly influenced by temperature and disinfectant concentration.

The experimental results evidence an effect of temperature and disinfectant presence on the corrosion mode and on the nature of the corrosion products.

At 70°C (25 ppm of sodium hypochlorite) corrosion was uniform and the main corrosion product was tenorite. At 50°C (25 ppm of sodium hypochlorite) corrosion was localized and the mainly corrosion product was malachite. Pitting corrosion only occurs after a long

incubation period. This incubation period corresponds to the evolution of the nature of the corrosion products on the copper surface, probably due to the transformation of cuprite film in products that would favor a localized degradation. Based on these results it has been proposed that solution was more corrosive at 50°C related with 70°C.

Our results also suggest that sodium hypochlorite concentration plays an important role on the corrosion mode and on the corrosion kinetics. Corrosion was localized at 50°C with 25 ppm of sodium hypochlorite while corrosion was uniform at 50°C with 1 ppm of sodium hypochlorite. The formation of corrosion products was accelerated at higher sodium hypochlorite concentrations under dynamic and static conditions. We assume the presence of a disinfectant concentration threshold beyond which pitting corrosion could appear at 50°C. This localized corrosion appears after a long incubation period, depending on the composition and agitation of the solution, the temperature, pH and concentration of disinfectant.

The addition of a corrosion inhibitor was also tested. The results suggest that the corrosion inhibitor is slightly effective. The corrosion inhibitor delayed the pitting apparition on samples aged at 50°C with 25 ppm of sodium hypochlorite.

Obviously, these conclusions are limited to new (non-aged) copper pipes and to water qualities close to those tested. Future works should investigate several water qualities. Short-term effects may be quite different from the long-term effects, so, another relevant investigation should prolong tests.

Acknowledgments

This work was supported in part by VERI. The authors are grateful to N. Berthelot and Y. Goubeyre for their help.

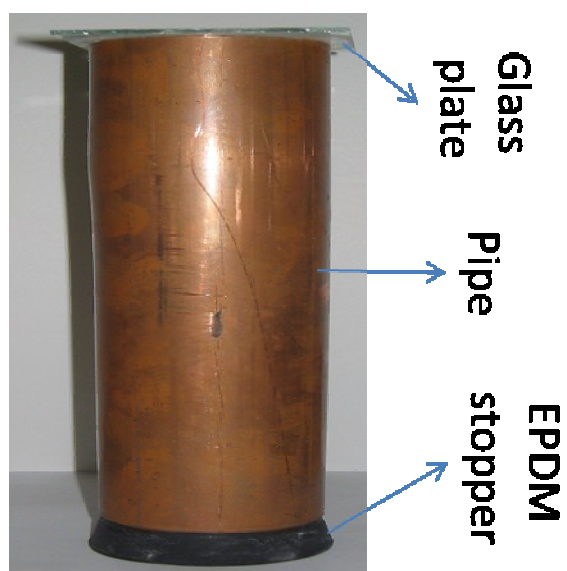


Figure 1: Sample filled with the solution (static ageing configuration).

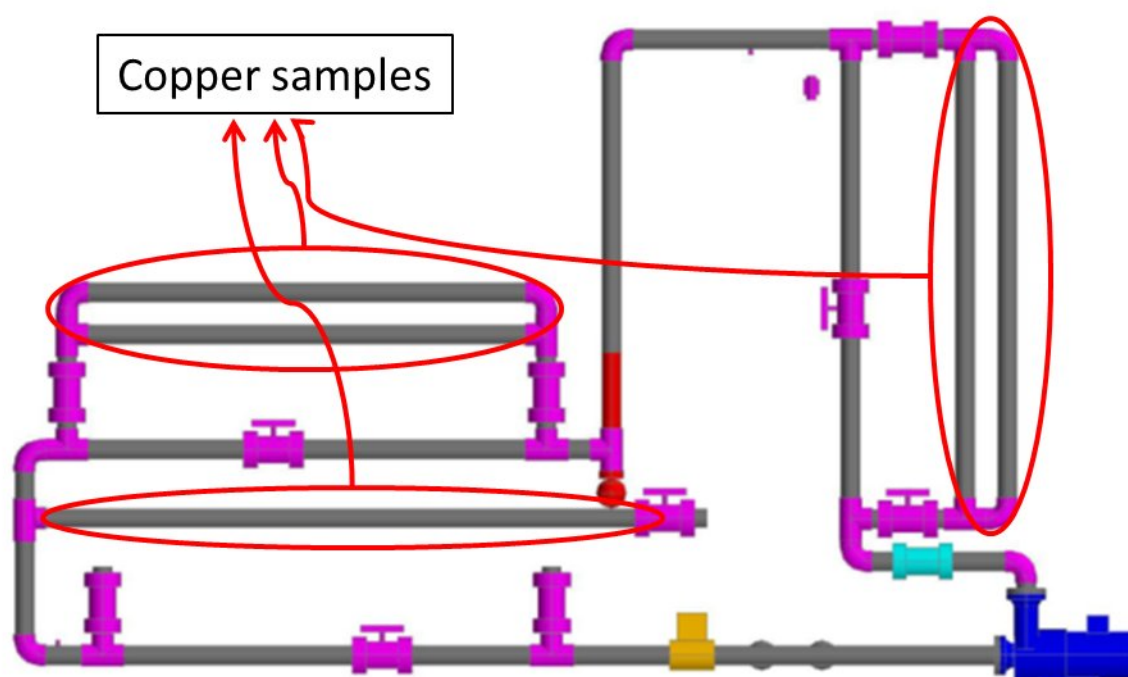


Figure 2: Schematic of the recirculating flow pipe loop.

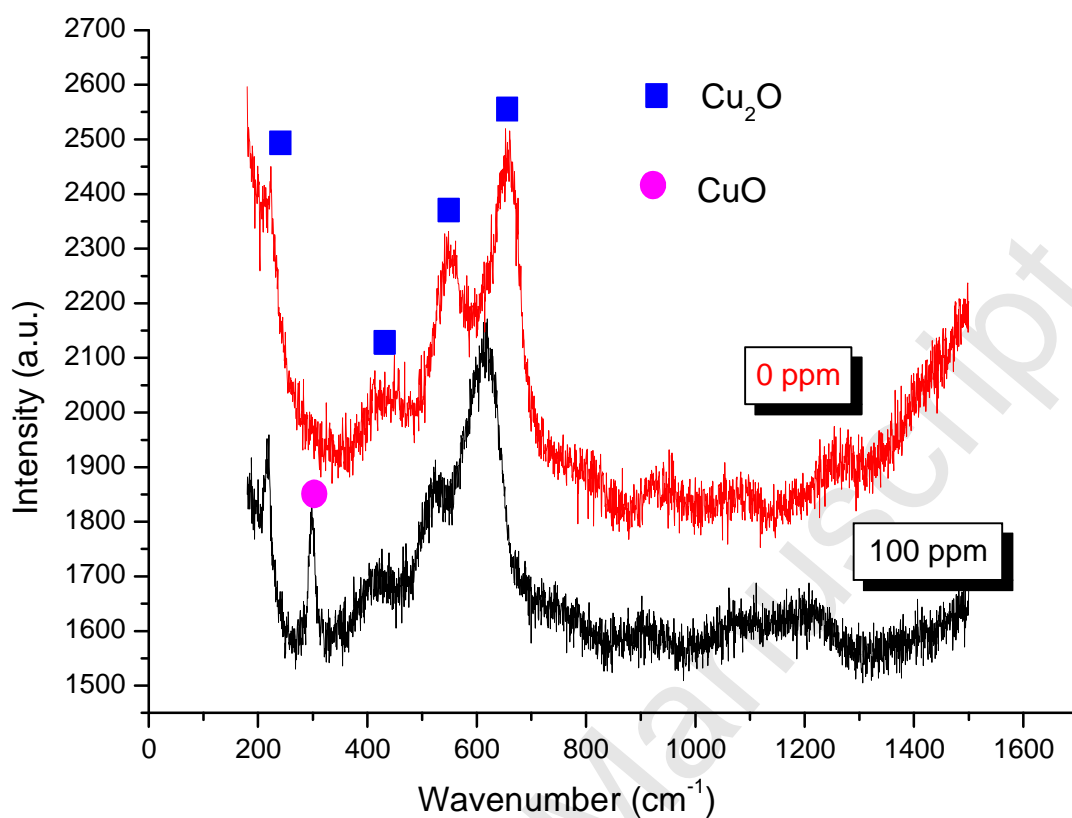


Figure 3: Raman spectra of samples aged during 45 days at 0 and 100 ppm

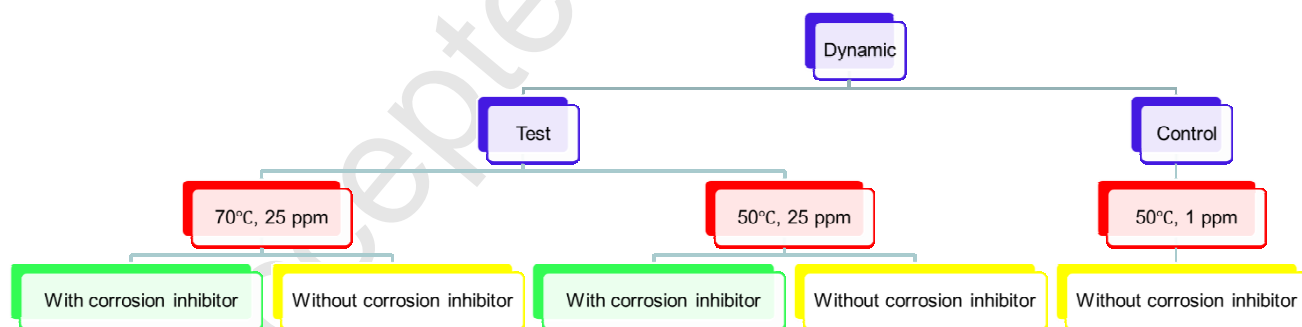


Figure 4: Summary of dynamic ageing conditions.

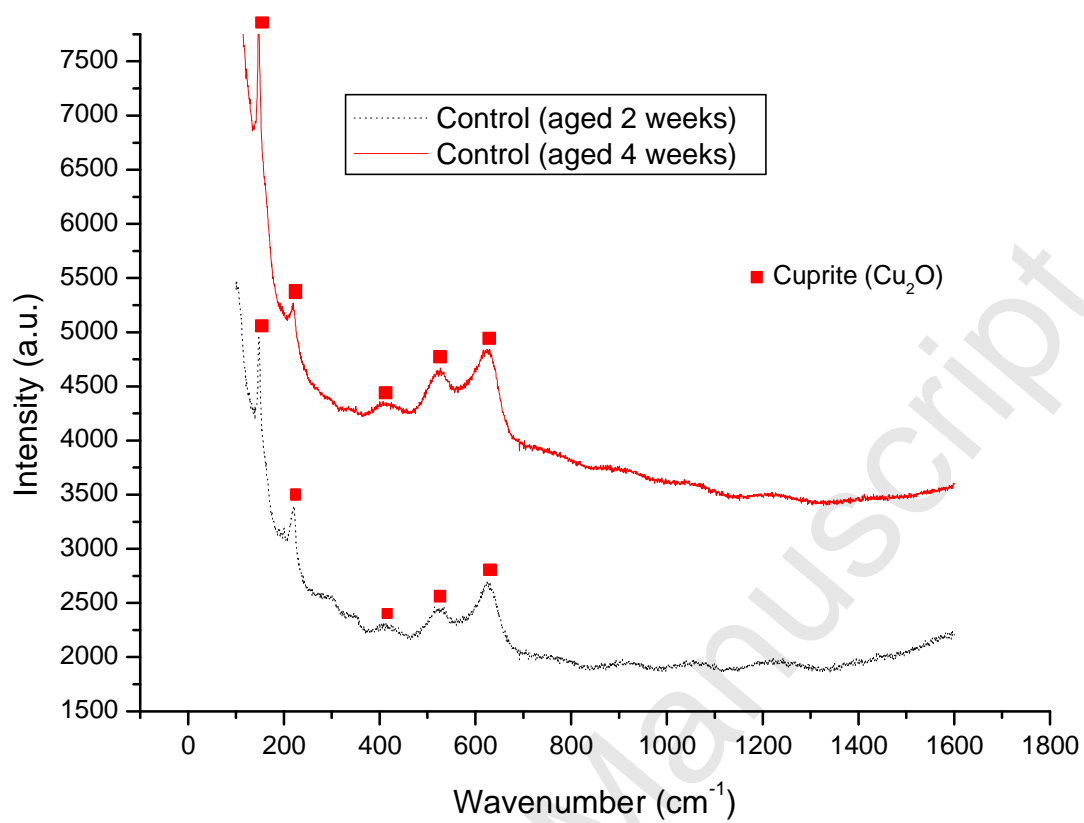


Figure 5: Raman spectra of copper samples exposed during 2 and 4 weeks to the reference conditions at 50°C and 1ppm of sodium hypochlorite.

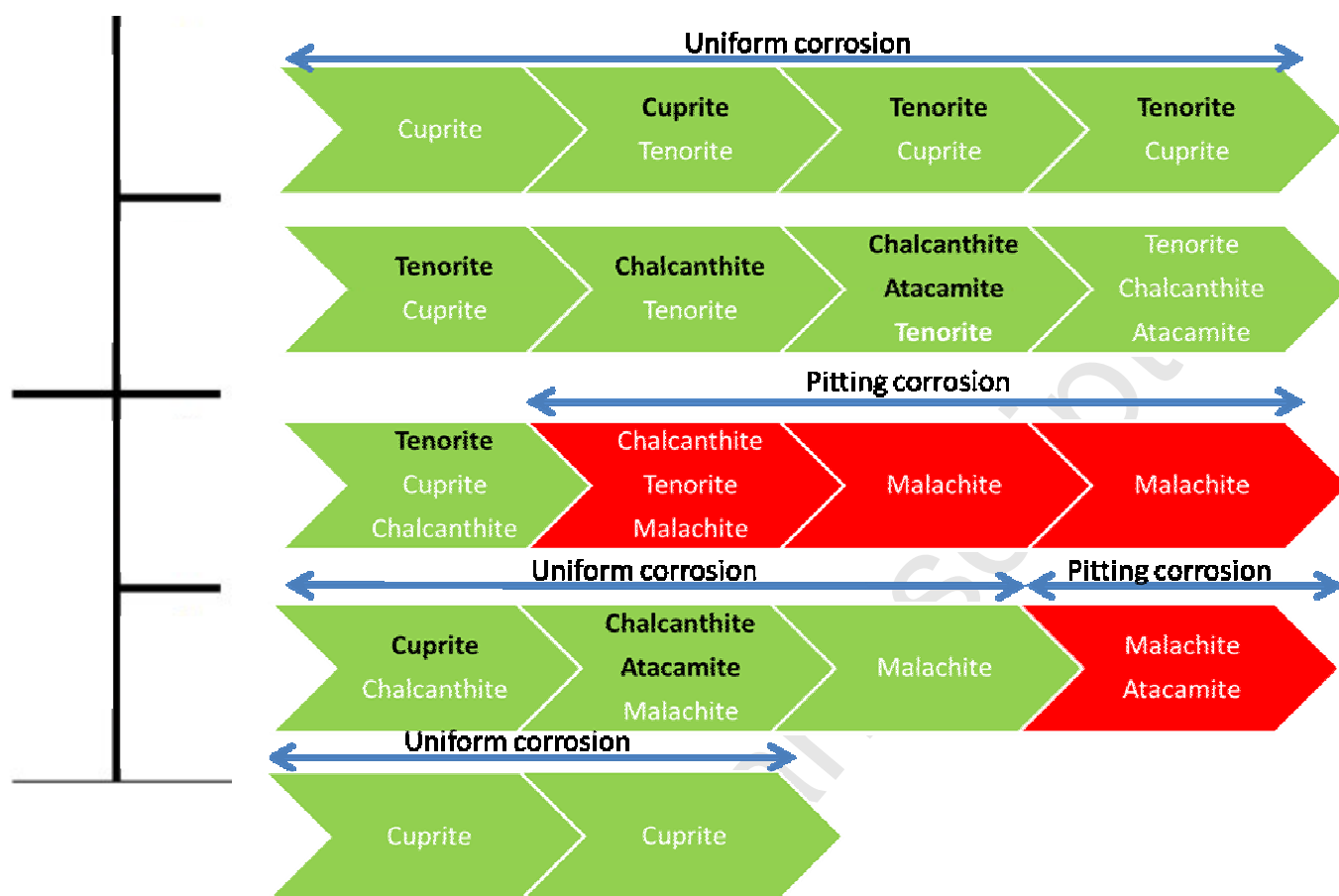


Figure 6: Sequence of appearance of corrosion products as a function of the ageing condition (major corrosion products in bold).

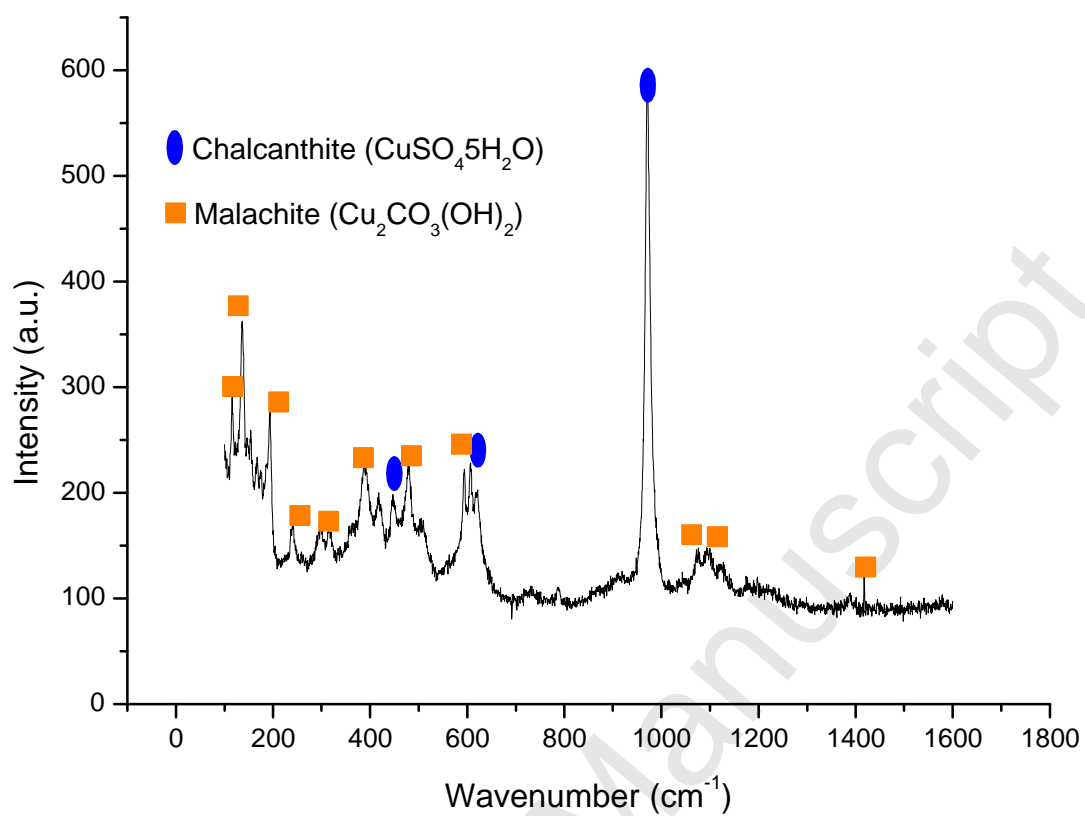


Figure 7: Raman spectra taken on the mound of the pit of a sample aged at 50°C and 25 ppm without corrosion inhibitor.

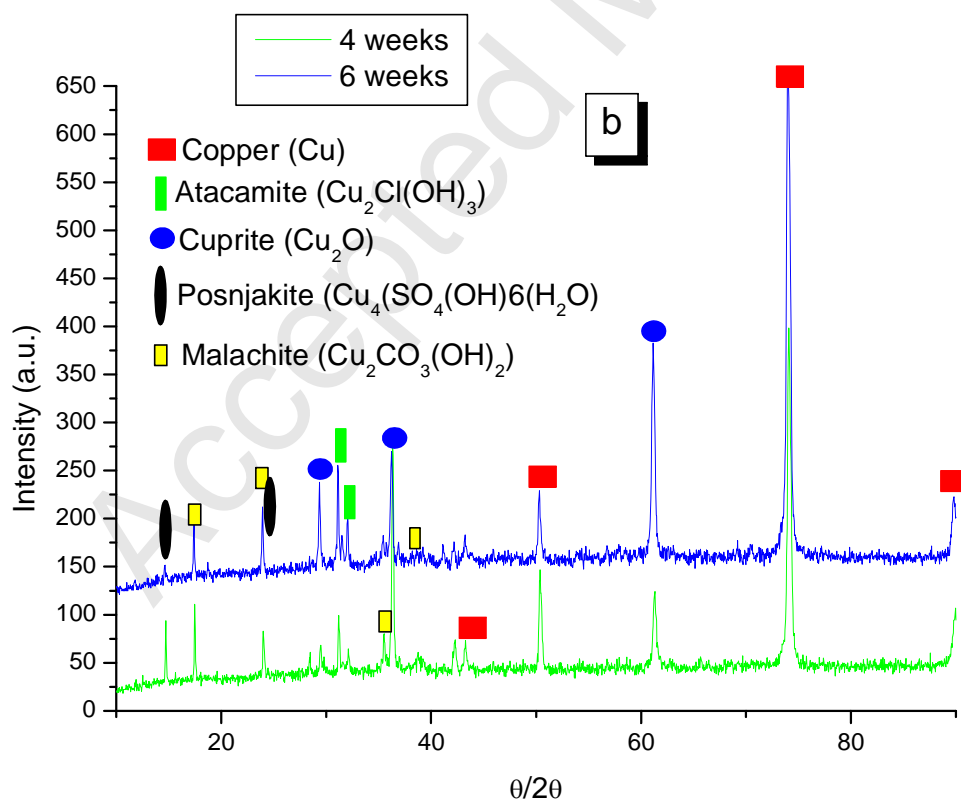
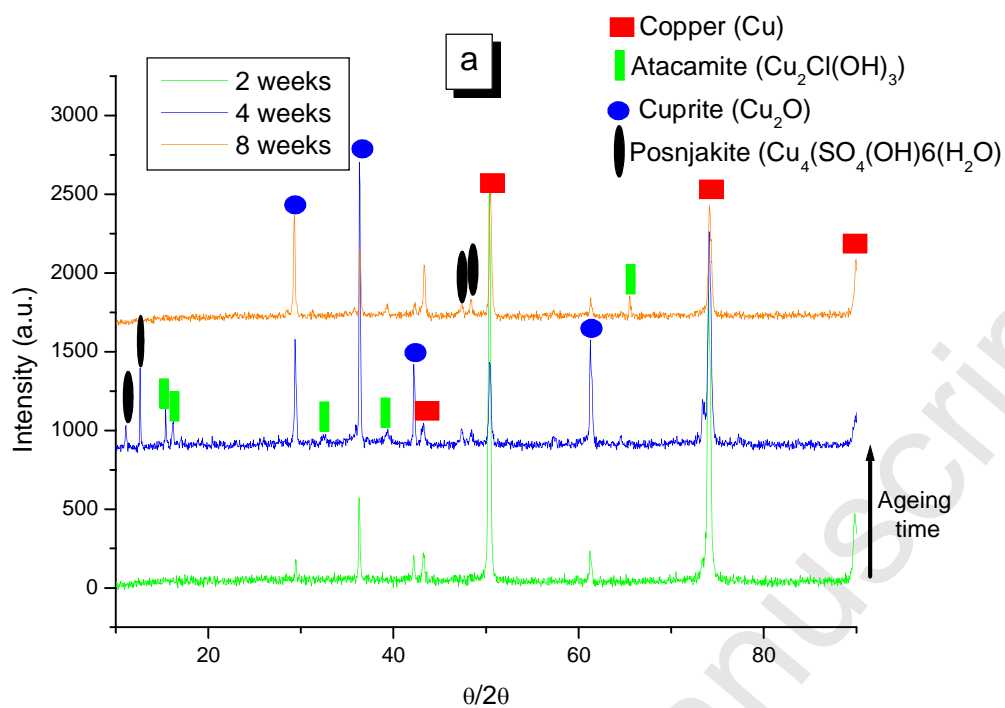


Figure 8: XRD patterns of samples aged with the corrosion inhibitor.

Condition	Concentration (mg.L ⁻¹)	Temperature (°C)	pH	Ageing time (hours)	Résultats	Réf.
Static	6 (NaClO)	Ambient	5 et 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 et 1,5 (NaClO)	4, 20, 24 et 60	7 et 9,5	4320 (6 months)	<ul style="list-style-type: none"> ➤ 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)	<ul style="list-style-type: none"> ➤ 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]

Table 1: Studies about corrosion of copper pipes.

Ions	Na ⁺	Mg ²⁺	K ⁺	Ca ²⁺	Cl ⁻	(SO ₄) ²⁻	(NO ₃) ⁻	OH ⁻
Concentration (ppm)	20.4	5	4	45	20	45	9	0.4

Table 2: Nantes tap water composition.

	Control loop	Test loops	
		Condition 1	Condition 2
Circulation velocity (m.s ⁻¹)	0,3±0,04		
Flow rate (L.min ⁻¹)	4±0,3		
Temperature (°C)	50±2	70±2	50±2
Disinfectant concentration (ppm)	1±0,2	25±2	
Retention time (hours)	10±0,5		
Pressure (bar)	0,8±0,2		
pH	7,2±0,2		

Table 3: Conditions of dynamic tests.

Samples	Temperature (°C)	[Cl ₂] (ppm)	pH
Control	70	0	8
Test		100	9,3

Table 4: Summary of tests realised under static conditions.

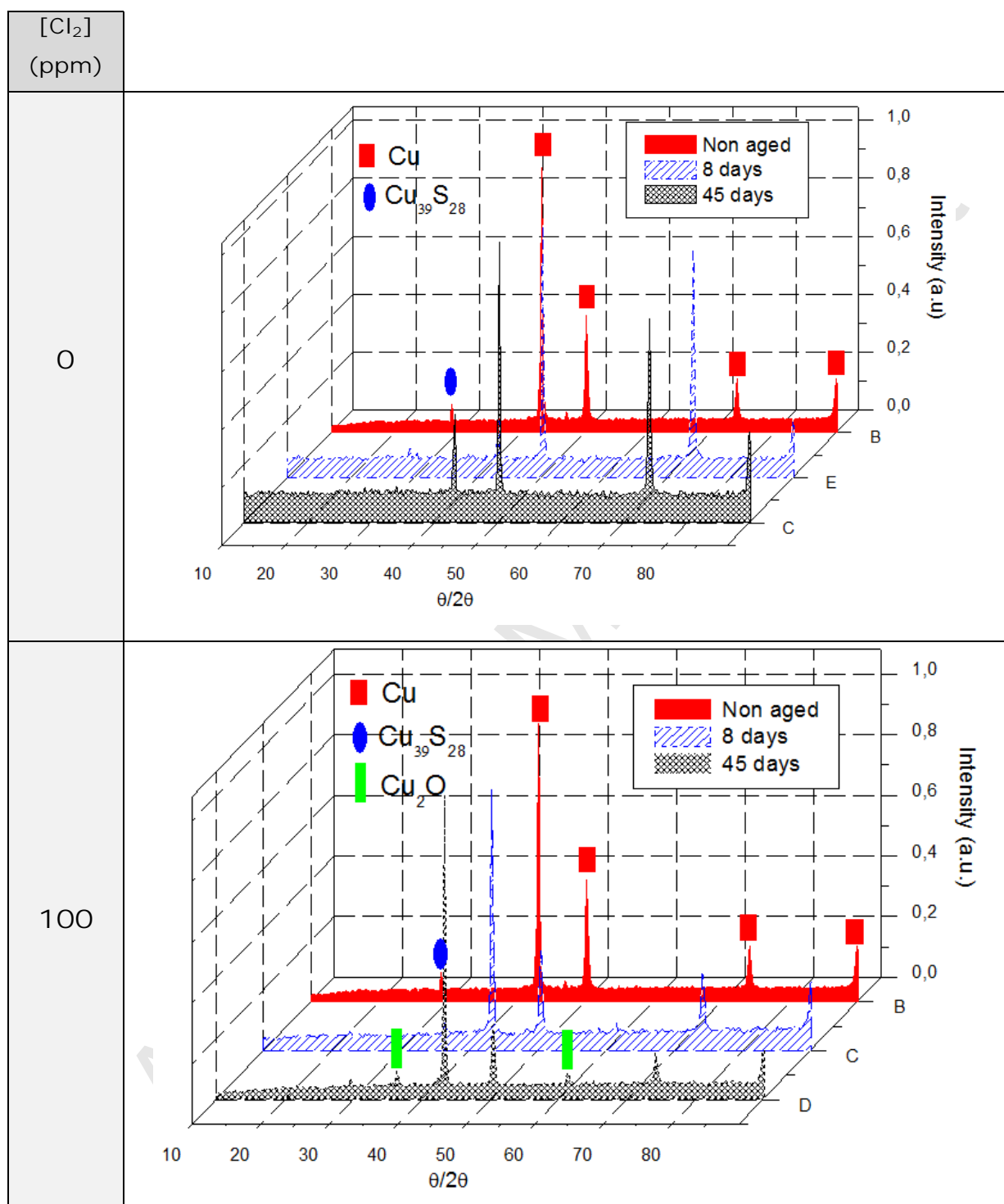


Table 5: XRD patterns of copper samples filled with solutions with 100 ppm and 0 ppm sodium hypochlorite concentrations.



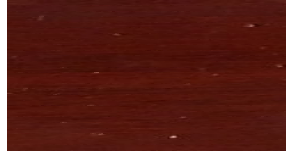

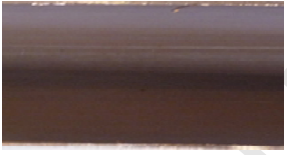




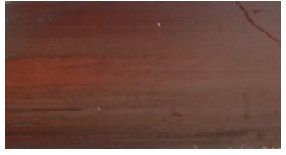


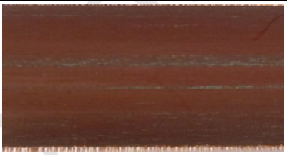






[Cl ₂] (ppm)	T (°C)	Corrosion inhibitor	Ageing time (weeks)			
			2	4	6	8
25	70	With				
		Without				
	50	With				
		Without				
1	50	Without			 Non aged	

Table 6: Examples of internal appearance of samples aged under dynamic conditions.

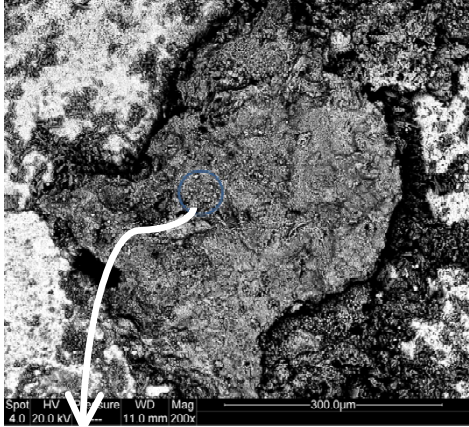
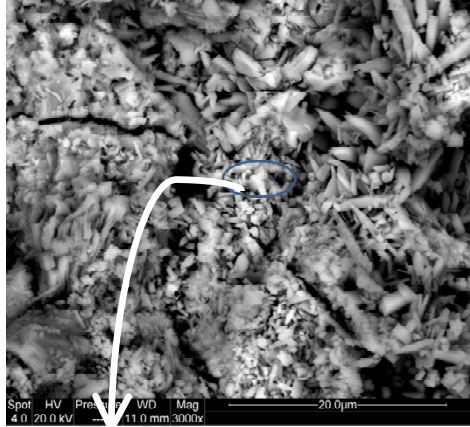
Ageing time (weeks)	4	8																								
Magnification	X200	X300																								
Image																										
EDX analysis	<table border="1"> <thead> <tr> <th>Element</th> <th>Atomic %</th> </tr> </thead> <tbody> <tr> <td>C</td> <td>35</td> </tr> <tr> <td>O</td> <td>37</td> </tr> <tr> <td>S</td> <td>2</td> </tr> <tr> <td>Cl</td> <td>1</td> </tr> <tr> <td>Cu</td> <td>25</td> </tr> </tbody> </table>	Element	Atomic %	C	35	O	37	S	2	Cl	1	Cu	25	<table border="1"> <thead> <tr> <th>Element</th> <th>Atomic %</th> </tr> </thead> <tbody> <tr> <td>C</td> <td>19</td> </tr> <tr> <td>O</td> <td>48</td> </tr> <tr> <td>S</td> <td>4</td> </tr> <tr> <td>Cl</td> <td>3</td> </tr> <tr> <td>Cu</td> <td>26</td> </tr> </tbody> </table>	Element	Atomic %	C	19	O	48	S	4	Cl	3	Cu	26
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Table 7: SEM images and EDS analysis of pits formed on samples aged without corrosion inhibitor at 50°C and 25 ppm of sodium hypochlorite during 4 and 8 weeks.

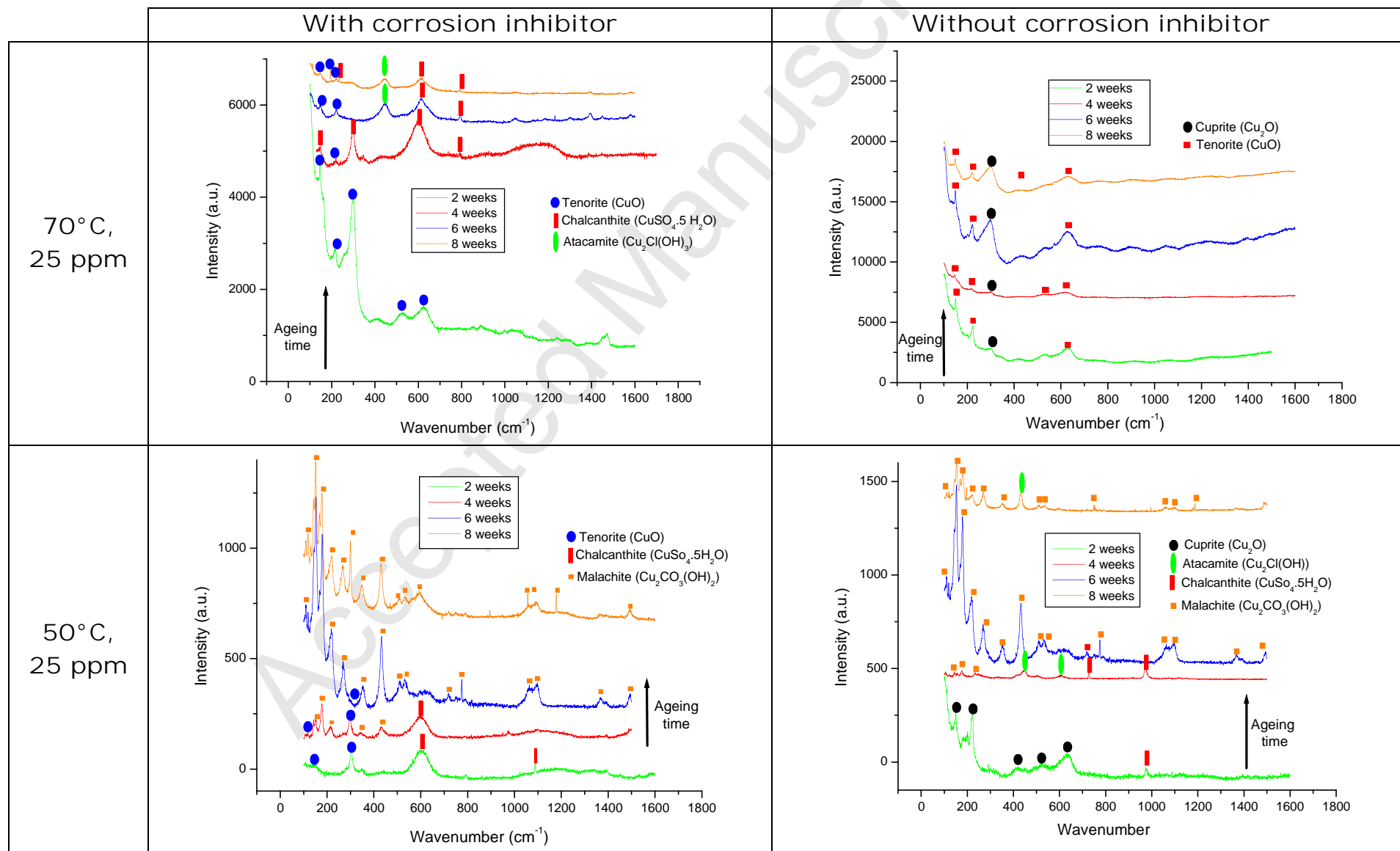


Table 8: Raman spectra of test samples.

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Accepted Manuscript

Highlights :

- Impact of disinfectant treatment on the durability of copper pipes.
- Synergy between disinfectant concentration and temperature
- Pitting corrosion of copper associated to the corrosion products formation on copper.

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