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EXPERIMENTAL EVIDENCE FOR ENHANCED COPPER RELEASE FROM HOUSEHOLD DRINKING COPPER PIPES UNDER DIFFERENTS HYDRODYNAMIC CONDITIONS

TOMAS E. OLIVARES

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Advisor:

RODRIGO A. CIENFUEGOS

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A mi familia, mi esposa y mis gatas...

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RESUMEN

Este trabajo presenta un estudio de la liberación de cobre en cañerías de cobre, usando datos experimentales para desarrollar un modelo conceptual del proceso de incorporación de cobre a la columna de agua y posterior transporte. Los experimentos fueron conducidos para determinar la influencia del flujo en la liberación de cobre bajo dos condiciones: superficies abióticas y superficies bióticas. Para las condiciones bióticas se midieron diferencias entre el cobre total y el disuelto dependiendo del flujo después de la primera descarga. Para condiciones abióticas, se analiza la correlación entre la liberación de cobre y el término fuente requerido para cerrar el balance de masa a través del tiempo.

En la etapa experimental se comparan distintas cañerías con caudales diferentes, y se analiza si la liberación de cobre aumenta a medida de que el caudal es mayor, o si este sólo influye en el tiempo necesario para desplazar una cantidad fija de cobre disponible para ser transportado. Los valores de caudal oscilan entre los 1 y 10 L/min y presentan números de Reynolds entre 1,000 y 11,000 aproximadamente, representativos de régimen laminar, transición a turbulento y turbulento.

Para condiciones abióticas, los resultados presentados indican que existe una influencia en la tasa de la liberación de cobre, de acuerdo con el cambio en un término fuente, en un balance de masa proveniente de una ecuación de advección-difusión. Este cambio refleja, bajo las condiciones establecidas, que el flujo desplaza en el tiempo una cierta cantidad de cobre determinada por las condiciones químicas preestablecidas, pero que en sí, no parece producir un aumento neto en la cantidad de cobre incorporado al flujo.

Para condiciones bióticas se observan diferencias comparado con los experimentos abióticos: en la concentración total, en la relación entre el cobre total y el cobre disuelto, y en la magnitud requerida para el término fuente para cerrar el balance de masa.

ABSTRACT

This paper presents a study of copper release and its relation to flow parameters in copper pipes using experimental data to produce a conceptual model of the copper release to the bulk flow and the transport processes at play. Experiments were conducted to determinate the influence of flow on copper release, under two conditions: biotical and abiotical surfaces. For biotical pipes differences were measured between dissolved and total copper depending on the flow characteristics after the first flush. For abiotical conditions, we analyze the correlation between copper release and the change in the required source term to comply with the mass balance equation over time.

In the experiments, different pipes and flow conditions were compared to assess if the total released copper was dependent on the flow discharge, and if the flow discharge had an influence on the time or volume of water required to remove a constant amount of copper that would be available to be transported. Flow discharge values were comprised between 1 and 10 L/min, to cover laminar, transition to turbulence, and turbulent flow conditions.

For abiotical conditions, experimental results show an influence on the rate of copper release, according to a change in a source term in the mass balance equation. This change indicates that copper is transported by the action of the flow, but there is no evidence that the flow increases the net amount of total copper incorporated into the bulk flow, for these specific conditions.

For biotical conditions, differences were observed in the experiments compared with abiotical experiments: in the amount of the released mass copper, total and dissolved copper ratio, and in the magnitude of the source term required to comply with the mass balance equation.

1. INTRODUCTION

1.1 Background

Copper has been extensively used in pipeline systems in Chile and worldwide, because of its durability, relative low cost, and antibacterial properties against some organisms that are harmful to humans (e.g. *Salmonella enterica* (Keevil, 2001, Faundez et al., 2004)). However, copper corrosion and its release from the pipe wall to the water by the combined effect of bio-chemical processes and flow hydrodynamics may produce several types of damages in infrastructure (Athanasiadis et al., 2010), and in household pipes. This latter may result in an increase of copper concentration with important consequences to human health (e.g. liver diseases (Smallwood et al., 1968)), and for other species, like fishes, with concentrations under 0.01 mg/L (Oskarsson and Norrgren, 1998).

Although copper is an antibacterial material, biofilm formation is well documented (Keevil, 2004, Critchley et al., 2004, Pavissich et al., 2010). Biofilm in copper could increase slowly in time with corrosion after 120 days (Jang and Ka, 2011), depending on environmental conditions. Typical studies about bio-chemical conditions do not include the flow as a key factor. However, some researchers have studied copper release in the bulk flow under different flow conditions: (Lehtola et al., 2006) studied the effect of flow velocity in the formation of biofilms, and showed that rapid changes in water flow could increase the bacterial and copper concentration in the bulk flow for laminar flow Reynolds number (*Re*) typically under 2,200. On the other hand, (Aisopou et al., 2011) showed the

importance that unsteady flow mixing have on water quality for different substances and biofilms. (Calle et al., 2007) studied the influence of flow condition in copper pipes and proposed a hydrodynamic model for copper release which demonstrated that diffusive transport from the boundary to the bulk flow is not the main copper release mechanism from copper pipes.

During the initial stages of pipe flushing after stagnation, hydrodynamic processes may also influence corrosion and the release of copper into the water, increasing its concentration in the bulk (Calle et al., 2007, Vargas et al., 2010, Merkel and Pehkonen, 2006). However, very little work has been done to clarify the mechanisms responsible for flow induced copper corrosion in domestic plumbing pipes and the quantification of the additional amount of copper mass that can be released under the action of flowing water. The different types of flow induced corrosion that have been identified in the literature are (Heitz, 1991, Efird, 1977, Yabuki, 2009, Nesic and Postlethwaite, 1991): i) Mass-transport controlled corrosion, ii) phase-transport controlled corrosion, iii) erosion-corrosion, and iv) cavitation, in which hydrodynamic processes are likely to enhance pipe corrosion. In particular, through series of experiments performed in sea water copper pipes, (Efird, 1977) found that the threshold in shear stresses for erosion-corrosion is over 9.4 N/m^2 . Under steady state conditions this value is reached for Reynolds numbers over 30,000, which is almost 3 times higher than typical household pipes. Other researchers suggest that flow could also enhance other corrosion processes,

such as pitting, but this would depend on both, flow and water quality, including pH and chlorine (Custalow, 2009, Lytle and Nadagouda, 2010).

Although pipe hydrodynamics is a well-known topic, there are many unanswered questions regarding how the flow in the conduit affects pipe corrosion and copper release, especially at Reynolds number typical of laminar and transition to turbulent conditions (Re < 10,000) which are more often found in domestic water installations. The Chilean regulation for water supply systems fixes the pressure head between 147.1 and 490 KPa in range, and in household installations a typical maximum value for conduit flow discharge is 12 L/min, which in turn implies an approximately Reynolds number, Re~12,000, for 3/4 inches pipes. A tap opening process produces a rapid acceleration of the water contained in the pipes thus generating unsteady shear stresses that might be responsible for an increase of copper release. The transition from laminar to turbulent conditions occurs in pipes between $Re \approx 2,100$ and $Re \approx 4,000$ where the exact threshold value would be strongly dependent on initial conditions (Faisst and Eckhardt, 2004). The flow in this regime shows complex structures and processes that makes it complex to analyze even when reaching the steady state (Eckhardt et al., 2007). For high Reynolds numbers, near-wall roughness influence is larger on the flow dynamics because the viscous sub-layer is thin enough and turbulent structures have sufficient kinetic energy to affect the corrosion products (Wharton and Wood, 2004). It has also been reported that flushing in pipes aged in biotic conditions could result in a higher copper concentration in the bulk flow than the one obtained after stagnation in abiotic conditions (Boulay and Edwards, 2001). By the other hand, chemical parameters in tap water are also important. It has been reported that high carbonated water could also affect the rate of corrosion by forming a passivating layer which could protect copper surface (Feng et al., 1996, Cong et al., 2009). Temperature is also relevant in the corrosion process by affecting the rate of corrosion because at higher temperatures copper corrosion increases; the orientation of pipes also might affect the mixing process of water into the pipe affecting the rate of corrosion (Rushing and Edwards, 2004, Boulay and Edwards, 2001).

Maximum concentration of released copper is typically found after 7-12 hours of stagnation (Merkel et al., 2002) due to oxygen consumption. Similarly, the study of aged pipes flushed under different flow conditions has shown that the release of copper might be dependent on flow hydrodynamics; indeed, at the initial stages of water flushing through pipes, an increase in the copper concentration has been observed, evidencing that flow hydrodynamics might enhance an additional loss of material from the pipe surface (Calle et al., 2007, Vargas et al., 2010). Experimental results suggest that during these events, part of the increase in copper concentration is due to the presence of nanoparticles in the bulk water, probably induced by shear stresses under unsteady conditions (Vargas et al., 2010), but not necessarily in the form of the so-called erosion-corrosion, which is due to high velocities under fully turbulent flows, and is increased by irregular surfaces and exposure of the raw material which were not observed in this study.

The quantification of the link between flow hydrodynamics and copper release in domestic pipes is difficult owing to the transient nature of the initial stages of flushing events which imply a transition from laminar to turbulent conditions. An indirect technique used to measure the flow influence on copper release to the bulk water includes measuring outlet concentrations from pipe experiments and flow volume (V) (Calle et al., 2007, Vargas et al., 2010). Moreover, it can be assumed that outlet copper concentrations can be correlated with global flow parameters such as mean shear stresses () or mean flow velocity (u). Mean shear stresses are usually computed from the cross-section averaged flow velocity or by pressure head differences along the pipe (P) (Viola and Leutheusser, 2004, Streeter et al., 1998, Yabuki, 2009).

In the present work, we report new experimental results on copper release from aged pipes under different flow conditions by taking care in controlling hydrodynamic, physical, biological and chemical characteristics of the flowing water. Our aim is to quantify the rate of copper release from the pipe surface to the bulk flow and to link it to hydrodynamic variables. For that purpose, we carry out flushing experiments on copper pipes measuring the total mass of dissolved copper transported by the bulk flow out of a control volume, and several hydrodynamic parameters, such as flow discharge and pressure fluctuations within both edges of the pipe system. The relation between flow hydrodynamics and copper release is analyzed combining experimental observations and an integral form of a copper mass balance equation resulting in an advection-diffusion transport model. The objective of this study is to determinate the influence of flow velocities on copper release by experimental procedures including flow and copper measurements, and control volume analysis. Experimental procedures are described first; second, experimental results from different measurements are presented, and analysis and findings obtained from experiment and conceptual modeling are given.

2. MATERIALS AND METHODS

2.1 Experimental Set-up

An experimental set-up for the analysis of pipe systems subjected to stagnant and flushing conditions was prepared in the Hydraulic laboratory of the Pontificia Universidad Católica de Chile. The experimental set-up is schematically depicted in Figure 2-1. The water was supplied from a tank with constant water head of 42 cm to a PVC pipe of length 1.5 m and 0.0195 m of external diameter (Figure 2-1 C). The copper pipe test section was located after the PVC pipe and consists of a 1.0 m length pipe with an internal diameter of 0.0195 m providing a total volume capacity of 0.3 L (1 V_0). The total length of the experimental set-up was 3.2 m. At the end of the piping system, the water was collected for copper analysis. The piping system had three ball valves for flow control and was equipped with a continuous electromagnetic flow discharge measuring device and two high response pressure sensors (TP1, TP2, Figure 2-1B) at each end of the copper pipe to be described later.

The experimental methodology was defined as follows: (a) an aging process of the tested pipes, (b) a stagnation period, (c) flushing and collection of samples and hydrodynamic data, (d) data analysis and post-processing. Before each test, the copper pipes were prepared using a standard cleaning protocol (Jeria, 2009): Pipes were cleaned during 2 minutes with NaOH 0.1 M to remove particles, then, 3 times with tap water, and finally 3 times with MilliQ water.



Figure 2-1.- Experimental Set-up (A) Aging process set-up, (B) Nozzle, (C) Flushing Experimental set-up.

Before reaching the testing section, we ensured that the flow velocity profile was fully developed. For a laminar boundary layer, the required development length can be estimated from $L_e=0.03*R_e*D$ where D is the pipe diameter (Wharton and Wood, 2004); for turbulent flows the following relationship is commonly used: $L_e=4,4*R_e^{1/6}*D$ (Munson et al., 2002). Using, D=0.0195m, $Re\approx2,000$ and 10,000 respectively, we get $L_e=1.17$ m (laminar), and $L_e=0.39$ m (turbulent). Hence the minimum length of the pipe must be 117 cm at 20°C. To ensure full development under steady conditions, an additional pipe length was considered to reach 150 cm.

2.2 Flow stagnation experiments

To examine different aging times and flow conditions, eight experiments were conducted (Table 2-1). For tests #1 to #6, and prior to the stagnation-flushing experiments, an aging process was conducted during 6 weeks with a synthetic water using MilliQ water and NaHCO₃ (99.7% chemical grade, Merck KGaA,

Germany) to adjust HCO_3^- to 14mM and pH=8.5. This procedure was aimed to induce the formation of a copper carbonate hydroxide film (Vargas et al., 2010). For the experiments, pipes were prepared, and kept in horizontal position connected to a peristaltic pump (Cole-Parmer Model No.7553-75), and connected to a tank (Figure 1(A)). The water inside the pipe was replaced every 48 hours because oxygen is consumed in nearly 50 hours (Vargas et al., 2009). The operating flow discharge for water replacement was set to 0.36 L/min in order to avoid hydrodynamic effects on the pipe surface (high shear stresses and turbulence). The estimated Reynolds number for this operation was Re= 432.

Experiment	Aging time	Aging water
#1	6 weeks	By protocol
#2	6 weeks	By protocol
#3	6 weeks	By protocol
#4	6 weeks	By protocol
#5	6 weeks	By protocol
#6	6 weeks	By protocol
#7	more than 2 years	Tap water (Calle et al., 2007)
#8	more than 2 years	Tap water (Calle et al., 2007)

Table 2-1 Water and aging conditions of experiments

In tests #7 and #8, we used a real domestic pipe aged under uncontrolled environmental conditions for about 2 years. The tested pipe was installed in a house in the city of Talca, Chile. Water quality of tap water resulting from this aging process was previously documented and its aging process and the environmental conditions where the aging took place resulted in the development of a biotic film over the copper pipe surface (Calle et al., 2007). Once the pipe was removed from the domestic system for laboratory testing, we carefully controlled all other conditions in order to make it comparable with experiments #1 to #6, in terms of stagnation time and flow conditions.

Before conducting the flushing experiments, the water inside the copper pipe was stagnated for 7 hrs, at a temperature of $18 \pm 2^{\circ}$ C. During the flushing, there was a variable transient time, depending on the considered flow discharge, before reaching the steady state. The flushing operation was intended to mimic a typical tap opening in household systems. We tested steady conditions between 1.2 and 9.5 L/min, in laminar, transition and turbulent flows. Several samples were collected after a quick opening of the tap. Water temperature during the experiment was 16 \pm 2°C. The collected water samples, after flowing through the pipe system, were acidified at pH<2 with HNO₃ 65% for preservation. Total reflection X-ray fluorescence spectroscopy (TXRF) analysis of water samples was performed with the spectrometer S2 PICOFOXTM (Bruker AXS Microanalysis GmbH, Berlin, Germany), by triplicate, and the analysis of results were performed with software SPECTRA 6.1.1.2 (2007b). Further information on this protocol can be found in S2 PICOFOX[™] User Manual (2007a). For abiotic pipes experiments #1 to #6, the initial total copper concentration within the pipe (C_0) was measured in control pipe samples. Similarly, for all experiments the initial concentration of copper (C_{in}) on tap water was measured with this technique; its observed mean value was 0.014 ± 0.005 mg/L.

For experiments #5 to #8, dissolved copper was measured using a standard filtering protocol, similar to previous corrosion studies. Samples were sequentially filtered by a 0.45 μ m pore-size membrane and a 0.2 μ m pore-size membrane, and finally all samples were acidified with nitric acid for preservation.

2.3 Hydrodynamic conditions

To keep a constant head of water in the supply tank, an overflow spillway was installed in one side of it. Each experiment begins with the opening of the valve VT-1, filling the main pipe, and isolating the copper pipe. After that, valves VT-2 and VT-3 are opened simultaneously, while the water flowing out of the system is collected for copper content analysis.

Pressure within the copper pipe is measured through 2 nozzles of 2 mm diameter disposed near both edges of the pipe. Two KELLER pressure sensors, type PR-41X with a range of 0 to 0.1bar (TP1 and TP2 in Figure 2-1) are connected to the nozzles. A flow-meter PROMAG 50P 1.27 cm in diameter (Endress+Hauser, USA), was used to measure the flow through the system. The instrument set-up and the data acquisition were performed using the commercial software Signal Express (National Instruments, USA). Data sampling of flow discharge and pressure fluctuations was performed at 50Hz.

Experiment	Flow at	Reference	Reynolds
	steady state	Shear Stress	number at
	(L/min)	at steady	steady state
		state (N/m ²)	
#1	6.5	0.475	7,949
#2	5.2	0.393	6,359
#3	3.5	0.284	4,280
#4	1.2	0.029	1,419
#5	9.5	1.150	11,618
#6	3.2	0.170	3,914
#7	8.8	1.080	10,799
#8	0.8	0.021	1,027

Table 2-2. Hydrodynamic conditions of flow experiments

The water density and the diameter of the cooper pipe are assumed constant, thus flow velocity could be obtained from flow discharge measurements. Moreover, pressure fluctuations were measured at both ends so the instantaneous mean shear stress on the pipe wall could be computed with the following expression neglecting fluid and pipe compressibility(Streeter and Wylie, 1985):

$$\tau t = - \frac{\rho}{\pi D} \frac{dQ}{dt} + \frac{D}{4} \frac{\Delta P}{L_p}$$
(2.1)

where is the mean shear stress (N/m^2) along the pipe boundaries, t is the time (s),

is the water density (kg/m³), *D* is the pipe diameter (m), *Q* is the flow discharge (m³/s), *P* is the pressure drop along the pipe length (Pa), and L_p is the total length of the pipe (m).

To produce meaningful estimates of shear stresses from measured variables, the following post processing protocol was performed on raw flow discharge and pressure data using MATLAB®. First of all, a low-pass 4th order Butterworth filter with cut-off frequency of 0.1 Hz was applied to clean it from the electrical noise (further information about this method can be found in the product documentation (The Mathworks, 2012). Next, current signals obtained from the electromagnetic flow meter and the pressure sensors were converted into hydrodynamic parameters (pressure and flow discharge) using previously calibrated equations for each instrument. The estimation of the term dQ/dt was produced through a 4th-order compact differential approximation (Ferziger and Peri, 2002) on the observed time signals of flow discharge, Q. Finally, the shear stress time series were computed from (2.1). Hydraulic experimental conditions are depicted in Table 2-2.

2.4 Surface analysis

To study the effect of flushing on pipe surface, microscopy and elemental composition of surface of different flushed and unflushed pipes were conducted. Scanning electron microscopy (SEM) and Energy-dispersive X-ray spectroscopy (EDS) were done with a LEO 1420VP scanning electron microscope coupled to an Oxford 7424 solid-state detector. Several coupons of 0.5x 0.5 cm were cut from the central part (in length) of the pipes. Sample preparation was performed under a laminar flow chamber (Labtech, model LCB-0122H), and kept hydrated until the following steps. Coupons were treated with critical point drying and coated with a thin gold film. This treatment has already been applied in similar studies (Vargas et

al., 2010) with the aim of preserving microbial cells and corrosion by-product structures (Carr et al., 1996, Schadler et al., 2008).

2.5 Copper mass transport equation within copper pipes

To describe copper concentration in the bulk flow, an 1D advection-diffusion mass transport equation were used, and it is written as follows (Rubin and Atkinson, 2001):

$$\frac{\mathrm{dC}}{\mathrm{dt}} + u\frac{\mathrm{dC}}{\mathrm{dx}} - \mathrm{E}_{\mathrm{L}}\frac{\mathrm{d}^{2}\mathrm{C}}{\mathrm{dx}^{2}} = \mathrm{S}$$
(2.2)

where C=C(x,t) is the cross-section averaged copper concentration within the pipe, u=u(t) is the cross-section averaged velocity in the pipe (computed from the instantaneous flow discharge and the pipe section neglecting compressibility effects in the water and pipe), E_L is a longitudinal diffusion coefficient, S=S(x,t) is the rate at which copper is incorporated into the bulk flow (the source term), and x is longitudinal space variable. As a first approximation, longitudinal dispersion was neglected in this equation assuming that this process does not have the time to influence copper concentration distribution within the 1 meter-long pipe, because copper diffusion coefficient is about 0.72 x 10⁻⁵ cm²/s (Newman, 1973) which is considered negligible in front of the advective flow transport. It was thus assumed that advection in the flow direction is the dominant transport process. The source term, *S*, should then explain the additional copper mass release from the pipe surface to the bulk flow at the time scales considered in these experiments. The

and copper concentration in a control volume analysis for flushing experiments starting at rest and reaching a steady state flow condition.

Spatially integrating (2.2) within the pipe, between x=0 y $x=L_p$, to perform a control volume analysis, and neglecting the longitudinal dispersion process, results in the following equation:

$$<\frac{dC}{dt}> + \frac{u C_{out} - C_{in}}{L} = < S >$$
(2.3)

where $\langle \rangle$ denotes a spatial average within the pipe length, C_{in} and C_{out} are the copper concentrations at the entrance and at the outlet of the pipe respectively, and the flow velocity is assumed to be independent of the space variable in agreement with the incompressibility hypothesis. Furthermore, assuming that the inflow copper concentration to the pipe is fairly constant, the first left hand side term can be estimated from:

$$< \frac{dC}{dt} > \approx \frac{1}{2} \frac{dC_{in}}{dt} + \frac{dC_{out}}{dt} = \frac{1}{2} \frac{dC_{out}}{dt}$$
 (2.4)

Hence, the spatially averaged copper mass release from the pipe surface to the bulk flow can be estimated from experimental measurements of flow variables and copper concentration using the following expression:

$$\langle S \rangle = \frac{1}{2} \langle \frac{dC_{out}}{dt} \rangle + \frac{u C_{out} - C_{in}}{L}$$
(2.5)

This relation will be the basis for the estimation of copper release from measured variables that will be presented in the next section. We use $S_{nd} = \frac{\langle S \rangle * Vo}{Q * C_o}$ to get a dimensionless form of

$$\frac{\langle s \rangle * V_O}{Q * C_O} = \frac{V_O}{Q * C_O} \left(\frac{1}{2} < \frac{dC_{out}}{dt} > + \frac{u C_{out} - C_{in}}{L} \right)$$
(2.6)

3. **RESULTS AND ANALYSIS**

3.1 Surface Analysis

EDS was performed for experiment #5, #6 and the control pipe, i.e. abiotic conditions (Figure 3-1). According to the results of the EDS, analysis revealed the following composition: Oxygen=19.56 elemental Carbon=25.88, and Copper=54.56 (atomic percentage) and 7.60, 7.65 and 84.75 respectively (weight percentage). These results suggest the presence of copper carbonate hydroxides, probably malachite, which is preponderant under studied conditions in a 5 to 9 pH range, according to (Merkel and Pehkonen, 2006). SEM analysis for inner surfaces in abiotic experiments under different flows: experiment #5 (Figure 3-2A), #6 (Figure 3-2B) and control pipe (Figure 3-2C), showed no differences in morphology among experiments without visible large cavities on the surface. In contrast, SEM analysis for the real domestic pipe surface, experiment #7 and #8, showed randomly distributed cavities with different sizes (Figure 3-2D). The surface seems to be heterogeneous with visible corrosion products and cavities smaller than 5 μ m (Figure 3-2E). Furthermore, in a closer analysis it is confirmed that a bacterial biofilm is attached to the corrosion products (Figure 3-2F). Similar conformation was seen in previous experiments with a pipe extracted from the same system but under laminar flow (Calle et al., 2007). The surface analysis shows that under biotic conditions, surface's heterogeneity could enhance copper concentration in bulk flow by detaching particles with different sizes, which was not seen under abiotic conditions.



Figure 3-1. SEM images and EDS analysis. Purple rectangle indicates location of EDS

analysis. A) Sample Experiment #5, B) Sample Experiment #5 control.



Figure 3-2. SEM analysis for biotical and abiotical experiments.(a) experiment #5 surface at 500x (b) experiment #6 surface at 500x, (c) Control pipe surface at 500x. (d) Experiment #7 at 500x. (e) Experiment #7, presence of cavities along the surface. (f) Experiment #7, presence of bacterial biofilm at 30000x.

3.2 Copper release measurements: Abiotic tests

Total copper carried by the bulk flow was measured in the supply tank (Cin) and at the outlet of the pipe (Cout), with T-XRF. Cin was measured before conducting the flushing experiments obtaining an average value of $C_{in}=0.014 \pm 0.005$ (mg/L). For abiotic experiments, #1 to #6, the average value for initial cooper inside the stagnant pipe was of $C_0=0.322 \pm 0.032$ (mg/L). Figure 3-3 shows the total copper concentration for these experiments. All data collapse into a single curve evidencing a consistent pattern. We used dimensionless parameters for concentration (C/C_0) and flow volume (V/V_0) to transform equation C(V) $C_0 * f(V)$ into (3.1). This curve could be fitted to the experimental data using a least square error procedure with an adjustment coefficient R²=0.913 and a root mean square error of RMS=0.704. These results were consistent with previous experiments since copper concentration decreases as the volume of water flowing out of the pipe increases (Vargas et al., 2010), and they also suggest that the total amount of copper incorporated to the bulk flow follows a similarity law, where the total amount of copper mass available to be released to the bulk flow is constant, so that the hydrodynamics only controls the time scale at which this process occurs, being faster under higher velocities. The copper concentration evolution of water flowing out of the pipe can be represented by the following equation, which it is drawn in Figure 3-3(b):

$$\frac{c_{out}}{c_o} = 0.546 - 0.5 \tan \mathbb{Z} \left(\frac{v}{v_o} - 0.84 * 3.04 \right)$$
(3.1)



Figure 3-3. Results for experiments #1 to #6 (a) Copper concentration in time. (b) Dimensionless result for copper concentrations flowing out of the pipe and least square function adjustment.

To quantify the copper mass release from the pipe surface to the bulk flow, we estimate the required source term from the mass transport equation in

(2.5). The copper concentration in the bulk flow C_{out} in this equation is computed from the fitted relationship presented in (3.1), while flow velocity is estimated from instantaneous flow discharge measurements. Results for the different tested conditions are presented in Figure 3-4(b) as a function of the dimensionless flowing water volume V/V₀. It is seen that different curves for $\langle S \rangle$ are obtained for different flow conditions as seen in Figure 3-4(a), but they collapse into a single curve as shown in Figure 3-4(b). These two figures represent the fact that differences in concentration curves are represented by the time and velocity, but not necessarily by differences in the total mass released.



Figure 3-4. Time evolution of the copper source term. (a) Dimensionless source term for different flows, and flowing volumes. (b) Dimensionless source term for different flows in time.



Figure 3-5. Source term as a function of the acceleration of the flow produced by the valve opening for different experiments. Linear adjust is plotted, with y=2.614*x + 0.015796,

Most of the copper incorporated into the bulk flow is released in the transient state. There is a variable release rate in the first part of the experiments up to 1.5 V/V_o. Significant differences in the magnitude of the source term, $\langle S \rangle$, among different flow conditions are also observed. The slowest flow has a maximum value for the source term $\langle S \rangle_{max}$ =0.0186 mg/L-s for 0.221 V/V_o, equivalent to 0.06 L. For the fastest flow, $\langle S \rangle_{max}$ =0.0976 for 0.4465 V/V_o equivalent to 0.13L. Figure 3-4(b) shows that most of the copper mass is released once the volume of stagnated water has left the pipe (V/V_o~1). Similarly, the volume of water that has to flow through the pipe in order to reach the steady state differs among the experiments. In Figure 3-5 we present a linear relationship between the peak values of $\langle S \rangle$ for different flows, and v*/t*, which represents the effect of transient states produced by the valve opening (as an estimation of the acceleration of the flow), where v* is velocity at steady state and t* is the time needed to reach the steady state. As $\langle S \rangle$ increases, this acceleration term also increases, evidencing a consistent pattern.

The experimental results presented so far suggest that under the studied conditions there is a visible effect on the time scale of copper release from the pipe surface to the bulk flow, though there is no significant difference in the total mass released among the experiments. The latter implies that for abiotic conditions, the total mass copper incorporated to the bulk flow is indeed controlled more by the chemical conditions and by the aging process than by hydrodynamic conditions. Even though the mass is the same, the processes of copper release for low and high Reynolds numbers might be different, and also hydrodynamic conditions do affect the time scale at which this mass of copper is released. This finding could be relevant to improve protocols for copper measurements and water consumption in household installations.

3.3 Copper release measurements: biotic tests

For experiments #7 and #8 and according to Figure 3-7(b) and Figure 3-7(d) as expected, pipes with a biotic surface released a much larger copper mass to the bulk flow for similar flows and stagnation times than under abiotic conditions, which are presented in figure 3-7 (a) and (b). Copper concentration curves for the outflow water discharge are similar to the ones reported in (Calle et al., 2007) and they are different from the ideal plug-flow curves typically used as assumption to calculate copper concentration in bulk flow after stagnation (Lagos et al., 1999). There is no control pipe for abiotical conditions, for this reason, we assume C_o to be the total copper concentration of the first measured sample. Released copper can be represented using the following equation:

$$\frac{C_{out}}{c_o} = 0.546 - 0.533 \tan \mathbb{Z} \left(\frac{V}{V_o} - 0.73 * 2.68 \right)$$
(3.2)

Similar to abiotic samples, this curve could be fitted to the experimental data using a least square error procedure with an adjustment coefficient R^2 =0.883 and a root mean square error of RMS=0.297. Difference in RMS for biotic and abiotic experiments can be explained by the smaller amount of points to fit the equation. Differences with abiotic experiments are noticeable since higher copper concentrations along the curve are observed. In <S> curve values, maximum value for experiment #7 is 0.7803 mg/L-s about 8.4 times higher than experiment #5 (Figure 3-6); and for #8 is 0.167 mg/L-s, about 9.1 times than #4. Minimum copper concentration in biotic curve was not set to the zero, which is also documented (Calle et al., 2007, Jeria, 2009), because copper mass in the real domestic pipe is released after several liters of flushing. This means than $\langle S \rangle$ curve is not scaled by C_o only, but there are others processes involved. Moreover (Calle et al., 2007) proposed the idea that shear stresses associated to advective processes could be affecting release and increasing copper concentration for these pipes. On the other hand, the fact that an equation could be fitted to the experimental data of total copper implies that released copper mass is similar for the two different experiments independent of flow conditions; this idea is reinforced by observations on total copper mass as seen in Figure 3-7 (b) and (d) which is similar for experiments #7 and #8, with less than 4.7% of difference approximately.



Figure 3-6. Time evolution of the copper source term. (a) Dimensionless source term for different flows, and flowing volumes. (b) Dimensionless source term for different flows in time.

Experiment	Туре	Re	Total/filtered 0.45	Total/filtere d 0.22	Volume
#5	Abioti c	11,6 18	1.36	1.36	0.9 L
#6	Abioti c	3,91 4	1.10	1.21	0.9 L
#7	Biotic	10,7 99	3.47	2.96	0.9 L
#8	Biotic	1,02 7	1.13	1.77	1 L

 Table 3-1. Parameters for filtered samples



Figure 3-7.Total and dissolved copper. (a), (b) Curves of total and dissolved copper by a
0.45 and a 0.22 μm filter, for experiment #5 and #7 respectively. (c), (d) Curves of total and dissolved copper by a 0.45 and a 0.22 μm filter, for experiment #6 and #8, respectively.

To assess the differences between abiotic and biotic pipe surfaces, we compared total and dissolved copper in 0.9L. Results are presented in **;Error! No se encuentra el origen de la referencia.** In abiotic pipes, the total copper mass transported out of the pipe after 1 liter of water was about 100 μ g, for both Experiment #5 and #6. In contrast, under biotic conditions the measured total copper mass was nearly seven times larger, with values around 750 - 780 μ g as observed in Figure 3-7. Additionally, for biotic pipes, significant differences between dissolved and total copper were registered, for 0.45 μ m and 0.22 μ m (see **;Error! No se encuentra el origen de la referencia.**). The ratio between total and dissolved copper varied between 1, under laminar flow conditions, and 5 under

turbulent flow conditions. For the experiment #7 (high flow), the total copper released has a high part of particles with size larger than 0.45 μ m, and almost all dissolved copper is smaller than 0.22 μ m. For experiment #8 (low flow), almost all total copper is smaller than 0.45 μ m which implies smaller particles than in experiment #7. Dissolved copper mass for experiments #7 and #8 was higher than the abiotic experiments implying that dissolved copper did not come from the tap water only. This result shows that flow affects times scales of releasing but also affects the distribution of size particles in aged pipes under certain biotic conditions, probably induced by the effect of shear stresses over the pipe surface. In contrast, for the 6 weeks aged pipes, ratios do not show noticeable differences, thus suggesting that most of the copper particles are smaller than 0.22 μ m. The latter supports the findings of (Vargas et al., 2010) who hypothesized that the presence of nanoparticles could increase the observed dissolved copper.

4. CONCLUSIONS

A source term in the advection-diffusion copper mass transport equation was estimated for different experimental conditions on the aging process and Reynolds numbers. The maximum value reached for the source term seems to be proportional to the initial copper concentration inside stagnant pipes, and our results suggest that surface's heterogeneity imposed by the presence of a bacterial biofilm enhances the detachment of corrosion by-products increasing copper released into the drinking water.

For both conditions, increasing the velocity of the bulk flow resulted in a faster release of a certain amount of copper from the pipe surface, thus just changing the time scale of the process involved. The amount of total copper mass released is thus affected by the water quality parameters and the stagnation time, but no evidence of a higher total mass incorporated to the bulk flow was observed for these conditions.

Even though the total mass is the same, the release process of copper release for low and high Reynolds numbers might be different. This latter was observed in biotic pipes experiments in which flow conditions could generate differences in total and dissolved copper ratio for the same stagnation conditions. There were no differences for abiotic pipes.

Future work perspectives will be focused on studying and understanding release process of dissolved copper under both controlled biotic and hydraulics conditions, in order to generate a conceptual release model to understand the differences observed in this study.

BIBLIOGRAPHY

(2007a) S2 PICOFOX[™] User Manual. *Bruker Advanced X-ray Solutions, 2007.* Berlin, Germany, Bruker AXS Microanalysis GmH

(2007b) SPECTRA. *Software for Acquisition and Evaluation of XRF Spectra.* 6.1.1.2 ed. Berlin, Germany, Bruker AXS Microanalysis GmH.

Aisopou, A., Stoianov, I. & Graham, N. J. D. (2011) In-pipe water quality monitoring in water supply systems under steady and unsteady state flow conditions: A quantitative assessment. *Water Research*.

Athanasiadis, K., Horn, H. & Helmreich, B. (2010) A field study on the first flush effect of copper roof runoff. *Corrosion Science*, 52, 21-29.

Bergant, A., Simpson, A. R. & Tijsseling, A. S. (2006) Water hammer with column separation: A historical review. *Journal of Fluids and Structures*, 22, 135-171.

Bergant, A., Simpson, A. R. & Vitkovsky, J. (2001) Developments in unsteady pipe flow friction modelling. *Journal of Hydraulic Research*, 39, 249-257.

Boulay, N. & Edwards, M. (2001) Role of temperature, chlorine, and organic matter in copper corrosion by-product release in soft water. *Water Research*, 35, 683-690.

Brunone, B., Golia, U. & Greco, M. (1991) Some remarks on the momentum equation for fast transients. *Proc., Int. Meeting on Hydraulic Transients and Water Column Separation.* Valencia.

Calle, G. R., Vargas, I. T., Alsina, M. A., Pasten, P. A. & Pizarro, G. E. (2007) Enhanced copper release from pipes by alternating stagnation and flow events. *Environmental Science & Technology*, 41, 7430-7436.

Carr, J. H., Anderson, R. L. & Favero, M. S. (1996) Comparison of chemical dehydration and critical point drying for the stabilization and visualization of aging biofilm present on interior surfaces of PVC distribution pipe. *Journal of Applied Bacteriology*, 80, 225-232.

Cong, H., Michels, H. T. & Scully, J. R. (2009) Passivity and pit stability behavior of copper as a function of selected water chemistry variables. *Journal of The Electrochemical Society*, 156, C16-C27.

Critchley, M. M., Pasetto, R. & O'halloran, R. J. (2004) Microbiological influences in 'blue water' copper corrosion. *Journal of Applied Microbiology*, 97, 590-597.

Custalow, B. D. (2009) Influences of Water Chemistry and Flow Conditions on Nonuniform Corrosion in Copper Tube. Virginia Polytechnic Institute and State University.

Eckhardt, B., Schneider, T. M., Hof, B. & Westerweel, J. (2007) Turbulence transition in pipe flow. *Annual Review of Fluid Mechanics*, 39, 447-468.

Efird, K. D. (1977) Effect of fluid dynamics on the corrosion of copper-base alloys in sea water. *Corrosion*, 33, 3-8.

Faisst, H. & Eckhardt, B. (2004) Sensitive dependence on initial conditions in transition to turbulence in pipe flow. *Journal of Fluid Mechanics*, 504, 343-352.

Faundez, G., Troncoso, M., Navarrete, P. & Figueroa, G. (2004) Antimicrobial activity of copper surfaces against suspensions of Salmonella enterica and Campylobacter jejuni. *BMC Microbiology*, 4, 19.

Feng, Y., Teo, W. K., Siow, K. S., Tan, K. L. & Hsieh, A. K. (1996) The corrosion behaviour of copper in neutral tap water. Part I: Corrosion mechanisms. *Corrosion Science*, 38, 369.

Ferziger, J. H. & Peri, M. (2002) *Computational methods for fluid dynamics,* Berlin ; New York, Springer.

Greco, M., Brunone, B. & Golia, U. M. (1992) A Characteristics Model of Transient Friction in Pipes. *Journal of Hydraulic Research*, 30, 569-570.

Heitz, E. (1991) Chemomechanical effects of flow on corrosion. *Corrosion*, 47, 135-145.

Jang, H. J. & Ka, J. O. (2011) Effects of diverse water pipe materials on bacterial communities and water quality in the annular reactor. *Journal of microbiology and biotechnology*, 21, 115-123.

Jeria, G. A. (2009) Efecto de las condiciones hidrodinámicas en la liberación de cobre desde la interfaz sólido-líquido en cañerías de cobre corroídas biótica y abióticamente. *Departamento Ingenieria Hidraulica y Ambiental* Santiago, Pontificia Universidad Catolica de Chile.

Keevil, C. W. (2004) The physico-chemistry of biofilm-mediated pitting corrosion of copper pipe supplying potable water. *Water Science and Technology*, 49, 91–98.

Keevil, W. (2001) Antibacterial Properties of Cooper and Brass Demonstrate Potential to Combat Toxic E. coli O157 Outbreaks in the Food Processing Industry *Symposium on Copper and Health, held in CEPAL.* Santiago, Chile.

Lagos, G., Maggi, L., Peters, D. & Reveco, F. (1999) Model for estimation of human exposure to copper in drinking water. *Science of the total environment,* 239, 49-70.

Lehtola, M. J., Laxander, M., Miettinen, I. T., Hirvonen, A., Vartiainen, T. & Martikainen, P. J. (2006) The effects of changing water flow velocity on the formation of biofilms and water quality in pilot distribution system consisting of copper or polyethylene pipes. *Water Research*, 40, 2151-2160.

Lytle, D. A. & Nadagouda, M. N. (2010) A comprehensive investigation of copper pitting corrosion in a drinking water distribution system. *Corrosion Science*, 52, 1927-1938.

Merkel, T. H., Groß, H.-J., Wernera, W., Dahlkeb, T., Reichertera, S., Beuchleb, G. & Eberle, S. H. (2002) Copper corrosion by-product release in long-term stagnation experiments. *Water Research*, 36, 1547-1555.

Merkel, T. H. & Pehkonen, S. O. (2006) General corrosion of copper in domestic drinking water installations: scientific background and mechanistic understanding. *Corrosion Engineering Science and Technology*, 41, 21-37.

Munson, B. R., Young, D. F. & Okiishi, T. H. (2002) *Fundamentals of Fluids Mechanics*, John Wiley & Sons, Inc., New York.

Nesic, S. & Postlethwaite, J. (1991) Hydrodynamics of Disturbed Flow and Erosion Corrosion .1. Single-Phase Flow Study. *Canadian Journal of Chemical Engineering*, 69, 698-703.

Newman, J. S. (1973) *Electrochemical Systems.,* London, Prentice Hall International, Inc.

Oskarsson, A. & Norrgren, L. (1998) Copper pipes as a source of copper exposure in man and environment. *Environmental Reviews*, 6, 139-150.

Pavissich, J. P., Vargas, I. T., Gonzalez, B., Pastén, P. A. & Pizarro, G. E. (2010) Culture dependent and independent analyses of bacterial communities involved in copper plumbing corrosion. *Journal of Applied Microbiology*. Pezzinga, G. (1999) Quasi-2D model for unsteady flow in pipe networks. *Journal of Hydraulic Engineering-Asce*, 125, 676-685.

Rubin, H. & Atkinson, J. F. (2001) *Environmental fluid mechanics,* New York, Marcel Dekker.

Rushing, J. C. & Edwards, M. (2004) The role of temperature gradients in residential copper pipe corrosion. *Corrosion Science*, 46, 1883-1894.

Schadler, S., Burkhardt, C. & Kappler, A. (2008) Evaluation of electron microscopic sample preparation methods and imaging techniques for characterization of cellmineral aggregates. *Geomicrobiology Journal*, 25, 228-239.

Smallwood, R. A., Williams, H. A., Rosenoer, V. M. & Sherlock, S. (1968) Livercopper levels in liver disease: studies using neutron activation analysis. *The Lancet,* 292, 1310-1313.

Storli, P. T. & Nielsen, T. K. (2011) Transient Friction in Pressurized Pipes. II: Two-Coefficient Instantaneous Acceleration-Based Model. *Journal of Hydraulic Engineering-Asce*, 137, 679-695.

Streeter, V. L. & Wylie, E. B. (1985) Fluid mechanics, New York, McGraw-Hill.

Streeter, V. L., Wylie, E. B. & Bedford, K. W. (1998) *Fluid mechanics,* Boston, WCB/McGraw Hill.

The Mathworks, I. (2012) Product Documentation.

Vardy, A. E. & Brown, J. M. B. (1995) Transient, Turbulent, Smooth Pipe Friction. *Journal of Hydraulic Research*, 33, 435-456.

Vardy, A. E. & Brown, J. M. B. (2003) Transient turbulent friction in smooth pipe flows. *Journal of Sound and Vibration*, 259, 1011-1036.

Vargas, I. T., Alsina, M. A., Pasten, P. A. & Pizarro, G. E. (2009) Influence of Solid Corrosion By-products on the Consumption of Dissolved Oxygen in Copper Pipes. Corrosion Science. *Corrosion Science*, 51, 1030-1037.

Vargas, I. T., Pavissich, J. P., Olivares, T. E., Jeria, G. A., Cienfuegos, R. A., Pasten, P. A. & Pizarro, G. E. (2010) Increase of the concentration of dissolved copper in drinking water systems due to flow-induced nanoparticle release from surface corrosion by-products. *Corrosion Science*, *52*, 3492-3503.

Viola, J. P. & Leutheusser, H. J. (2004) Experiments on unsteady turbulent pipe flow. *Journal of Engineering Mechanics-Asce*, 130, 240-244.

Wharton, J. A. & Wood, R. J. K. (2004) Influence of flow conditions on the corrosion of AISI 304L stainless steel. *Wear*, 256, 525-536.

Wylie, E. B., Streeter, V. L. & Suo, L. (1993) *Fluid transients in systems,* Englewood Cliffs, NJ, Prentice Hall.

Yabuki, A. (2009) Near-wall hydrodynamic effects related to flow-induced localized corrosion. *Materials and Corrosion-Werkstoffe Und Korrosion*, 60, 501-506.

Zielke, W. (1968) Frequency-dependent friction in transient pipe flow. *Journal of basic engineering*, 90, 109.

ANNEX

Annex A: Hydrodinamic model

A.1 Background

In the previous section, we defined a mass balance equation for copper transport in the bulk flow and attempted to estimate the required source function in order to comply with the observed values of copper concentration in the outlet. Flow discharge and pressure time series were measured in the experiments in order to characterize the hydrodynamics. We now develop an unsteady model for flow in pipes in order to complete the analysis of the experiments. Continuity and momentum equations can be written in the following form (Streeter and Wylie, 1985):

$$\frac{dH}{dt} + \frac{a^2}{g} * \frac{du}{dx} + u \frac{dH}{dx} + u * \sin \vartheta = 0$$
(0.1)

$$\frac{dH}{dx} + \frac{1}{g}\frac{du}{dt} + \mathbb{Z}_f + \frac{u}{g}\frac{du}{dx} = 0 \tag{0.2}$$

where *H* is the piezometric head, *x* is the space variable, *g* is gravity, *u* is the average bulk flow velocity, ϑ angle of the pipe, *a* is the pressure wave celerity and *h*_f is the head loss per unit length. For practical applications in horizontal pipes, it is customary to neglect the convective terms and write the classical water hammer equations in the following form (Storli and Nielsen, 2011):

$$\frac{dH}{dt} + \frac{a^2}{g} * \frac{du}{dx} = 0 \tag{0.3}$$

$$\frac{dH}{dx} + \frac{1}{g}\frac{du}{dt} + \mathbb{Z}_f = 0 \tag{0.4}$$

For modeling purposes and to assess the accuracy of model results in comparison with experimental data, we test two different approximations of these equations. The first one follows from the rigid column model (RCM) which it just considers inertial effects.

The second is the classical water hammer model as written in the equations above. We use the method of the characteristics (MOC) to numerically integrate these equations.

In both models, the friction factor is calculated using an unsteady correction following as recommended by (Brunone et al., 1991).

A.2 Friction factor modeling

Head loss, h_f , is usually expressed as $\mathbb{Z}_f = \frac{fu^2}{D2g}$, and it can be discomposed into a quasi-steady term and an unsteady term such that $h_f = h_{f,q} + h_{f,u}$. Similarly, the friction coefficient is separated in quasi-steady and unsteady parts, $f = f_q + f_u$. This approach is well documented by (Pezzinga, 1999).

Friction factor, f, is calculated with the following equations depending on the characteristic of the flow. When calculation is done for each time in unsteady simulation, friction factor f is called quasi-steady, f_q . Under laminar flow conditions we use (0.5), and fo

$$f = \frac{64}{Re} \tag{0.5}$$

$$\frac{1}{\bar{f}} = -1.14 + 2\log(\frac{\epsilon}{D} + \frac{9.35}{Re\ \bar{f}})$$
(0.6)

with *D* the pipe diameter, and ε the wall typical roughness length.

To estimate the unsteady friction factor, f_u , many authors have proposed different parameterizations (Storli and Nielsen, 2011, Bergant et al., 2001, Greco et al., 1992, Wylie et al., 1993). In (Bergant et al., 2001) two models are compared: the Zielke model (Zielke, 1968), where friction term is dependent on instantaneous mean flow velocity *V* and weights for past velocity changes; and the Brunone model (Brunone et al., 1991), where the friction term is based on cross-sectional distribution of instantaneous flow velocity. Results and stability are similar for both models, but the second method is much simpler to code. For this reason Brunone model is developed here.

In Brunone model unsteady friction factor is calculated according to the equation:

$$f_u = \frac{k_b D}{u|u|} \left(\frac{du}{dt} - a\frac{du}{dx}\right) \tag{0.7}$$

where k_b is the Brunone friction factor coefficient and it can be analytically estimated using a shear decay coefficient C^* (Vardy and Brown, 1995), which is defined for laminar and turbulent flows based on experiments (Vardy and Brown, 2003):

$$k_b = \frac{\sqrt{C^*}}{2} \tag{0.8}$$

$$C = 0.00476$$
 (0.9)

$$C = \frac{12.86}{Re^{\log(\frac{15.29}{Re^{0.0567}})}}$$
(0.10)

Dependence of the Reynolds number of the shear decay coefficient is demonstrated for turbulent flow by (Bergant et al., 2001).

A.3 Rigid column model

The rigid column model is obtained when the fluid and the pipe are considered incompressible so velocity changes in the pipe length are neglected. The RCM reads:

$$\frac{dH}{dt} = 0 \tag{0.11}$$

$$\frac{dH}{dx} + \frac{1}{g}\frac{du}{dt} + \mathbb{Z}_f = 0 \tag{0.12}$$

If we use the friction factor model described above to compute the head loss term, h_f , we get:

$$\frac{dH}{dx} + \frac{1}{g}\frac{du}{dt} + \frac{f_q u^2}{D 2g} + \frac{k_b}{g}\frac{du}{dt} = 0$$
(0.13)

Assuming $\frac{dH}{dx} = \frac{dz}{dx} + \frac{1}{\rho g} \frac{dP}{dx}$, and integrating over x within the pipe length (subscript

1 for *x*=0 and subscript 2 for *x*=*L*) we obtain:

$$\frac{L}{g}\frac{du}{dt} = -z_2 - z_1 - \frac{1}{\rho g} P_2 - P_1 - \frac{f_q L u^2}{2g D} - \frac{L k_b}{g}\frac{du}{dt}$$
(0.14)

By developing the equation above taking $z_1=z_2$, and = g, we obtain the following rigid column equation for the pipe flow:

$$\frac{P_1}{\gamma} = \frac{P_2}{\gamma} + \frac{f_q L}{D} \frac{u^2}{2g} + \frac{L}{g} (1 + k_b) \frac{du}{dt}$$
(0.15)

Additional singular head losses produced by valves can be estimated as $F_k = K \frac{u^2}{2g}$, where *K* is a singular losses coefficient.

A.4 MOC model

The second hydrodynamic model based on the classical water hammer equations is integrated using the method of characteristics (MOC). Positive and negative characteristic equations are written in the following form, using i as iteration time; and p, position along the line (Bergant et al., 2006):

Along the C⁺ characteristic line, with +a = x/t:

$$\mathbf{H}^{+}: \left(H_{p}^{i} - H_{p-1}^{i-1}\right) + \left(\frac{a}{g} V_{p}^{i} - V_{p-1}^{i-1} + T_{f} = 0$$
(0.16)

Along the C⁻ characteristic line, with -a= x/t:

$$H: (H_p^i - H_{p+1}^{i-1}) - (\frac{a}{g} V_p^i - V_{p+1}^{i-1} - T_f = 0$$
(0.17)

 $T_{\rm f} \, \text{and} \, {T_{\rm f}}^*$ are shown in

the present time. Values used were , = 0.5.

$$T_{f}: \frac{a}{g 2D} \left[\beta f_{p-1}^{i-1} V_{p-1}^{i-1} V_{p-1}^{i-1}\right] + 1 - \beta f_{p}^{i} V_{p}^{i} |V_{p}^{i}|$$
(0.18)

$$T_{f}^{*}: \frac{a}{g 2D} \left[\alpha f_{p+1}^{i-1} V_{p+1}^{i-1} V_{p+1}^{i-1} \right] + 1 - \alpha f_{p}^{i} V_{p}^{i} |V_{p}^{i}|$$
(0.19)

Celerity defines the maximum time step by the equation t = x/a, which implies that two different wave celerity cannot be used in the model: copper pipe celerity is about 1,100 m/s, and pvc pipe celerity is about 300 m/s, according to the following classical equation (Streeter and Wylie, 1985), where E_y, Young module, D, Diameter, e, wall thickness, fluid density:

$$a^2 = \frac{\frac{K}{\rho}}{1 + \frac{KD}{E_y e}} \tag{0.20}$$

A.5 Application and calibration of the models

Boundary conditions

The boundary condition for the downstream end of the pipe is presented in

(0.21). In order to calibrate the flow curves under the investigated unsteady states, the singular head loss associated to the opening of the tap valve is represented by the function K_{tap} . This function will be adjusted with experimental data using the following form: K_{tap} (t) = Const₁ - Const₂ tanh(Const₃ t). With Const₁, Const₂, Const₃ constants to be adjusted; and t, the time. This form equation is chosen after testing different functions. The constant values depend on the opening procedure and on the flow conditions, so they have to be adjusted for each experiment.

$$V = K_{tap} \qquad \overline{2gH} \tag{0.21}$$

For the upstream end of the pipe, where the water head is maintained constant, we use H = $H_i - \frac{V^2}{2g} - K_0 \frac{V^2}{2g}$, with H_i=0.48m, K₀ constant of the pipe entrance.

Rigid column model computations

The integration procedure is defined as follows:

a) For calculation, a numerically solution is calculated for each point using boundary conditions, (0.15) and the MATLAB ode23 function, which is used to solve first degrees differential equations. Convergence factor is 10^{-4} . Further information is found in (The Mathworks, 2012).

b) Friction factor f_q is calculated iteratively using (0.5) and (0.6), and using it in (0.15). Notice than f_u is not into (0.15). For turbulent flow, k_b term is calculated with Reynolds number in t-1.

MOC model computations

The integration procedure is defined as follows:

a) First, all constants are defined. Number of nodes is set to 4 (It is possible to set this value in a higher value, but it produces a more intense computational work).

b) A first solution is computed using MOC equations H^+ , H^- and the quasisteady state friction factor f_q computed according to the classical Colebrook equation.

c) With first solution, temporal and space derivatives are calculated using numerical approximations for all times and positions, as follows:

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Left side derivative	$dV(j) = (-V_{j+1} - 4*0.5(V_j + V_{j+1}) - 3V_j)/\Delta J$
Middle side derivative	$dV(j) = (0.5(V_i + V_{i+1}) - 0.5(V_{i-1} + V_i))/J$
Right side derivative	$dV(j) = (3V_j - 4^*0.5(V_{j-1} + V_j) + V_{j-1})/J$

d) In a second step, the unsteady friction f_u is calculated using (4.7), derivatives calculated for the first solution and the quasi-steady friction factor f_q estimated in the previous step.

e) (0.16) and (0.17) are solved for each point and time, using calculated values.

Model Adjustment

For both models, the calibration process for valve operation and singular losses are similar and it is described in the following.

a) The first parameter adjustment for the tap opening is performed using steady state conditions (t>20 sec). The steady state head losses in the conduit are calibrated adjusting K_{tap} and K_0 iteratively until flow calculated is fitted with experiments.

b) Once the model is able to reproduce steady state conditions, transition parameters are calibrated in transient state. Constants in $K_{tap}(t)$ equation are iteratively adjusted under the transient flow conditions until modeled discharge curves are fitted with experimental curves.

c) Once all constants are adjusted, source term is calculated with modeled flow and (2.5) and (3.1). As (3.1) is a parameterization of C_{out} calculated experimentally, the source term is an empirical function. After that, copper concentration C_{out}(t) is calculated with (2.3), using flow values calculated by the model. Finally, C_{out} (t) is compared with experimental outlet concentrations.

A.6 Results

Flow Estimations

Numerical calculation were performed over a laptop Sony VAIO PCG 7173L Intel mobile core 2 duo T6500 (2.1 GHz). Simulation time was over 1 minute, for both models. Several simulations were performed to determinate copper outflow concentration in flushing experiments. In first place, flow estimations are presented in Figure A-1 and Figure A-2, showing the flow discharge along time. Experiments #1-4 were modeled with RCM, and #5-8 with MOC. Basically, pressure conditions are a little different for experiment #1 - #4 than for experiments #5-#8, and the condition for #1-#4 are pretty different for programming in MOC. As the objective is to generate a concentration modeling with flow as a parameter, and the methodology of opening tap it was improved from experiments #1 .#4 to #5-8, it is not necessary to model first 4 experiment with MOC model. For both models flow curves are similar. In unsteady conditions (first 5 to 10 seconds) curves are not perfectly fitted to experimental data. In calibration, K_{tap} value is critical in the fitting process being an extra variable to adjust. In future experiments, this opening procedure could be improved, using mechanical/automatized control valves.



Figure A-1. Model vs experiment 1. Rigid column model.



Figure A-2. Model vs experiment #7. MOC model.

In both models opening term is very important to fit curve adequately. Both models have very similar results for flow modeling, being able to reach the steady state.

Pressure estimations

Two different opening operations were done. In the first case, experiments #1-4, valve 1 (copper pipe inlet) was opened at same time than valve 2 (copper pipe outlet). In the second case, experiments #5-#8, Valve 1 was opened a couple of seconds previously to the valve 2 opening. This change is shown in different pressure curves presented in Figure A-3 and Figure A-4. In experiment #8 there was a problem with the outlet experimental pressure measuring (TP2), and there is no data.

For MOC, pressure drop is higher in experimental conditions than in model, and oscillation seems to have lower wave celerity than typically used.

According to the different models, pressure head was estimated for each experiment. Major differences can be appreciated in the unsteady conditions. In both models several difficulties to achieve a realistic approach were seen: First, rigid model cannot reproduce oscillations in pressure, because it is based in velocity changes only. In MOC model, oscillation can be estimated, but it is difficult to calculate more than one wave celerity (copper pipe and PVC pipe have different values) which generates different results. In experimental conditions, valve opening velocity was a variable that could not be controlled since this operation can be done in many different ways, with the same result in steady state.



Figure A-3. Oscillations in pressure, experiment #1. Rigid column.



Figure A-4. Oscillations in pressure, experiment #1. MOC model.

Outlet Copper concentration estimations

Outlet Copper concentration can be estimated with both hydraulic models. Although pressure and friction are significant parameters, just velocity (flow) is used to calculate copper release. Two different approximations are tested: including <S> term, and not including <S> term. For first one, <S> term experimentally calculated is used. For experiments in abiotical conditions (experiments #1-#4), results are shown in Figure A-5 and compared with experimental measures; Experiments #5-#8 in Figure A-6. A different way to calculate copper release in similar experiments could be found in (Calle et al., 2007).

The effect of the incorporation of $\langle S \rangle$ is an increase in copper release in the first stage of the curves (the transient part of release curve) because it goes to zero in steady state This situation fit well for experiments #1-#4, but is not enough to the rest

of experiments. This means that a typical mass balance for a fixed amount of mass moving out just for effect of velocity need to be adjusted to estimate outlet concentration in this type of events.



Figure A-5. Copper concentration for different experiments, using a typical mass balance,

and a mass balance using <S> experimentally calculated.



Figure A-6. Copper concentration for different experiments, using a typical mass balance, and a mass balance using <S> experimentally calculated.

A.7 Modeling conclusions

Modeling outlet concentration in a pipe system needs not only velocity as a parameter, but a source term to fit correctly concentration curves. For this kind of modeling, both models (RCM and MOC) have good results in flow, and for that reason, similar results in concentration. In pressure head calculations, both models fail in unsteady cases. For concentration, using a <S> term improve results noticeable in transient state.

Annex B: TXRF protocol

B.1 Reagents

All reagents were of analytical purity grade. Gallium ICP Standard 1000 mgL⁻¹ Merck (Darmstadt, Germany) was diluted to 10 and 100 mgL⁻¹ and these three concentrations were used as internal standard. Dilutions were realized with HPLC water Merck (Darmstadt, Germany).



Figure B-7. Calibration curve

B.2 Procedure

Water sample previously acidified (pH<2, with HNO₃) was measured filtered or unfiltered for dissolved or total determination. 1 mL of the liquid sample was mixed with an internal standard, Gallium, and homogenized with vortex during 5 seconds.

Then 10 μ L was transferred onto a sample carrier and dried at least three hours using a heating plate (40-50°C) in a laminar flow chamber.

B.3 Measurement

Measurements were performed with a Bruker S2 PICOFOX TXRF with High Efficient Module configuration (2007a)(Bruker, GmBH, Germany). Features are showed in the Table B-2.

Power	37 W (max. 50kV, 0.75 mA)	
Monochromator	Multilayer, curved 17.5 eV	
Detector	Liquid nitrogen-free Silicon Drift, 30	
	mm2	
FWHM	<150 eV	
Autosampler	25 sampler carriers	
Size	450x590x300 mm	
Weight	37 kg	
Tube X Ray	Mo (Micro focus)	

Table B-2	TXRF	features
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The excitation parameters were 50 kV and 750 mA. Measurement time for all samples was 300s in triplicate. The spectrum was evaluated by Spectra 6.2 Software (Bruker, nGmBH, Germany). Quantitative analysis was performed by internal standard addition.

Annex C: Tap water

All experiments were developed in hydraulic laboratory. Experiments were done using tap water with the following chemical characteristics.

Composition	Concentration
Fluoride	0,075 ppm +/- 0,006
Chloride	98,180 ppm +/- 1,290
Nitrate	25,825 ppm +/- 0,300
Sulfate	260,081 ppm +/- 3,328

Table D-3. Tap water characteristics