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Modeling MIC copper release from drinking water pipes

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ABSTRACT

Copper is used for household drinking water distribution systems given its physical and chemical properties that make it resistant to corrosion. However, there is evidence that, under certain conditions, it can corrode and release unsafe concentrations of copper to the water. Research on drinking water copper pipes has developed conceptual models that include several physical-chemical mechanisms. Nevertheless, there is still a necessity for the development of mathematical models of this phenomenon, which consider the interaction among physical-chemical processes at different spatial scales. We developed a conceptual and a mathematical model that reproduces the main processes in copper release from copper pipes subject to stagnation and flow cycles, and corrosion is associated with biofilm growth on the surface of the pipes. We discuss the influence of the reactive surface and the copper release curves observed. The modeling and experimental observations indicated that after 10 h stagnation, the main concentration of copper is located close to the surface of the pipe. This copper is associated with the reactive surface, which acts as a reservoir of labile copper. Thus, for pipes with the presence of biofilm the complexation of copper with the biomass and the hydrodynamics are the main mechanisms for copper per release.

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1. Introduction

Copper is a material widely used in the world for manufacturing drinking water pipes due to its resistance to environmental conditions. However, copper corrodes under certain conditions, producing structural failure of water distribution systems [1,2] and increasing bulk water copper concentration to health threatening levels [3,4]. This has motivated scientists to study the corrosion on copper pipes to understand the involved mechanisms [4–10]. These studies have been focused primarily on: (1) the influence of water quality parameters (pH, temperature, oxygen, alkalinity, chloride, sulfate, phosphate and organic matter)[5,7,9,10]; (2) operating conditions (flow-stagnation cycles and age of the pipe) [6,11,12]; and (3) the release of copper into the drinking water. Although complex conceptual models have been developed, mathematical implementation of these models has not had major advances.

Most of the problems produced by copper release on water distribution systems are related to dissolved copper, the release of particulate corrosion products may also occur. These episodes are called "blue water" and they are frequently related to microbial activity [4,13–16]. The microbiologically influenced corrosion (MIC) generally occurs when colonies of copper tolerant bacteria (e.g. *Acinetobacter* sp., *Variovorax* sp., *Pseudomonas* sp.) colonize the inner wall of the pipe forming biofilms [17,18] preventing the formation of oxide layers and

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establishing anodic sites under the biofilm [17,19]. This phenomenon of copper pipe corrosion have been reported in domestic systems in different countries like Australia, Germany, Sweden and the UK [13–15,17,20,21].

The current trend on the development of mathematical corrosion models is to use empirical relationships derived from experimental observations of a process, which is influenced by a set of parameters [22,23]. However, the comparison between experimental results should be evaluated carefully because of the variability in the specific conditions of each study, such as temperature, operating conditions (i.e. stagnation, flow-stagnation), hydrodynamics (i.e. flow velocities), and area/volume ratio (i.e. ratio between the surface area of copper exposed to water and the volume of water in the pipe).

The objective of this study was to develop a conceptual and a mathematical model that reproduces relevant mechanisms of copper release in copper pipe systems subject to flow-stagnation cycles, when there's a presence of a biofilm. This work constitutes a first step to include the effects of hydrodynamic mechanisms on copper release in pipes subject to MIC.

2. Materials and method

2.1. Conceptual model

The conceptual model is based on a mechanistic approach, dividing this phenomenon in different processes, which occur at different temporal and spatial scales [8,11,15,23–26]. We present separately the

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conceptual model under flow and stagnation conditions in the presence of a heterogeneous biofilm.

2.1.1. Conceptual model under stagnation conditions

In the initial working stage of the pipe, a thin cuprite (Cu₂O) protective layer is formed on the inner wall. This layer constitutes the interface from which the release of copper ions is produced during stagnation [23,27,28].

The second stage corresponds to biofilm formation. It starts with the sorption in the pipe's wall of humic and fulvic substances of high molecular weight, which create a thin film of nutrients, this film complexes with copper ions and it is where the first cells of the biofilm adhere. Subsequently, the number of cells increases, and the microorganisms begin the production of metabolic products and exopolysaccharides (EPS), forming a matrix that agglomerates these cells and protects them against the Cu ions [8].

The third stage is the formation of a heterogeneous and reactive matrix, a mature biofilm. As the biofilm consolidates a heterogeneous structure is generated and the diffusion layer appears, such that the farthest areas from the biofilm surface (next to the pipe surface) have a lower nutrient concentration, as shown on the results obtained from mathematical models of heterogeneous biofilms [29–34]. Also the decline in nutrient concentration produces the formation of microchannels in the zones farthest from the biofilm surface, guaranteeing a nutrient supply for the different microorganism groups [35].

The structure of the biofilm formed on the copper surface is characterized by a few cells surrounded by abundant EPS, which are capable of inducing complexation of the copper ions through their carboxylic groups (COOH) [8,17,36]. The existing affinity between the Cu ions and EPS, along with the heterogeneity of the biofilm, are mechanisms that favor cuprosolvency because the removal of the Cu ions from the metal surface occurs in regions that are in direct contact with the biomass [17,37]. In this way, electrochemical microcells are established, in which the cathodic sites are located in the region adjacent to the biomass and the anodic sites are on the biomass surface, as shown in Fig. 1. At the anodic sites, the metallic copper is oxidized by the half-reaction $Cu^0 \rightarrow Cu^2 + 2e^-$; at the cathodic sites, O_2 is reduced by the half-reaction $1/2O_2 + 2H^+ + 2e^- \rightarrow H_2O$ [38].

Once the Cu^{2+} ions are released from the anodic sites, they are transported by diffusion mechanisms through the biofilm, as shown in Fig. 1. A small number of these ions precipitate to form solid corrosion products, such that the biomineralization of the biofilm occurs [17]. Another fraction of the ions undergoes complexation with the EPS, and a third fraction can cross the biofilm to reach the aqueous phase. Out of this latter fraction, a portion remains in solution and moves by diffusion mechanisms to form different organic and inorganic aqueous species; another portion forms precipitates or is incorporated into solid corrosion by-products on the pipe wall [11]. The identities of these aqueous species and solid corrosion by-products depend on the quality of the pipe water [7]. In general, the solid corrosion by-products that are formed in the presence of potable water are cuprite, tenorite, and malachite [11,17,23,28,39]. However, the physical-chemical conditions that can be established in the interior of the pipe will potentially induce the dissolution of these solid products and once again release copper into the aqueous phase.

The physicochemical mechanisms that produce the copper release occur at microscopic scales, which are defined by the biofilm and diffusion layer thickness. However, the released ions continue moving by diffusion and forming different species, which occurs at a macroscopic scale, as depicted in Fig. 1. These last two mechanisms occur on a macroscopic scale that is defined by the pipe's diameter, which is tens of millimeters wide. On a macroscopic scale, the diffusive transport elements depend on the pipe's area/volume ratio (area of the transversal section) as discussed in the literature. In fact, the narrow diameter of the pipes commonly used to distribute drinking water means that diffusive mechanisms control the transport of Cu from the pipe's wall toward the longitudinal core.

Even though the ratio between the dimensions of the macroscopic and microscopic scales is approximately 100, the group of mechanisms that cause the release and transport of Cu works jointly, causing the released copper to be distributed along the pipe's cross-section as long as the stagnation condition continues. By globally analyzing the presence of solid corrosion by-products and heterogeneous biofilms on the pipe's inner wall, it is possible to observe that these elements act like a reactive surface that controls the release of copper [40].

In terms of temporal scales, redox reactions and speciation occur in the order of seconds and minutes, precipitation reaction in the order



Fig. 1. Conceptual model and main processes considered for corrosion in copper pipes under the presence of biofilm during stagnation conditions.

of hours, days, weeks and months, and the diffusion mechanisms in the order of hours [23].

2.1.2. Conceptual model under flow conditions

During flow conditions, the velocity field formed within the pipe generates chemical and physical gradients, such as changes in water composition due to advective transport and shear stress due to viscosity, which occurs at a macroscopic scale. These mechanisms produce desorption of the labile copper and the release of nanoparticles from the inner surface of the pipe [12], increasing copper concentration in the water, as shown in Fig. 2. The flow that circulates through the pipe during the flow condition determines the cross sectional velocity profile. This profile has a parabolic form when the flow regime is laminar, in which viscous forces predominate over inertia. However, if the forces of inertia predominate, the flow is turbulent and the velocity profile has a logarithmic shape, which can be seen in Fig. 2. Flow conditions in domestic systems have a duration of the order of minutes, which is much lower than the stagnation condition [41]. Nevertheless, this time is enough to produce the extraction of the mass of copper released during stagnation.

2.2. Mathematical model

The development of the conceptual corrosion model established that during corrosion in a copper pipe in the presence of a biofilm, different physical, chemical, and biological mechanisms occur simultaneously but at different spatial and temporal scales. These processes present different levels of complexity, so simplifications are necessary to mathematically implement this model. Therefore, the mathematical model implemented has the following limitations:

a) The three-dimensional spatial mechanisms were simplified to reduce dimensional spatial scales. In this way, during stagnation conditions, the model with the presence of a biofilm is formulated in a two-dimensional Cartesian domain at the microscopic scale and is coupled to a one-dimensional domain in polar coordinates. During flow conditions, the model uses a two-dimensional domain in cylindrical coordinates for both the microscopic and macroscopic scales.

- b) The nucleation and growth mechanisms of malachite crystals are not considered in the model. These complex mechanisms require more extensive studies to determine the relationships between the concentrations of Cu^{2+} and CO_3^{-2} and the growth kinetics of the crystals.
- c) The complexation mechanisms of the Cu²⁺ ions with the natural organic matter were not included in the model. These mechanisms would have an effect on the nucleation and growth of the crystals on the pipe inner wall.
- d) The release of the Cu^{2+} ions from the pipe wall under stagnation conditions does not consider the electrochemical mechanisms that relate the O_2 and H^+ gradients at the pipe wall with the released copper. Instead, a constant release rate is set by assuming that the regions covered with biomass are anodic sites.
- e) For turbulent flows, the model does not include the presence of low velocities in the direction perpendicular to the pipe's longitudinal axis. Therefore, it does not consider the presence of vortices under flow conditions.
- f) Under flow conditions, the release of the Cu²⁺ ions sorbed onto the biomass are not associated with the kinetics that relates the shear stress and the concentration gradients with the copper release rate. Instead, an instantaneous release mechanism is used when flow is produced in the pipe.
- g) The model does not consider the detachment of biotic and abiotic solid nano-particles under flow conditions.

Considering these limitations, the mathematical corrosion model was posed by considering five main processes: 1) the transport of chemical species and substrates during stagnation, 2) the transport of chemical species during flow conditions, 3) the biofilm growth, 4) the speciation, and 5) the release of Cu^{2+} ions into the liquid. These processes occur at two spatial scales (microscopic and microscopic) and are divided into sub-processes, which were implemented independently and then coupled to construct the complete model. Table 1 presents the notation used in the implementation of the model. Table 2 shows the domain and spatial scale for each of these processes.



Fig. 2. Conceptual model and main processes considered for corrosion in copper pipes under the presence of biofilm under flow conditions.

Table 1

The notation used in the mathematical and numerical implementation of the model.

Symbol	Description	Dimension/unit
q	Exact solution for the substrate concentration in	[ML ⁻³]
	the mass balances under stagnation or flow.	
Q_i	Numerical solution of the substrate <i>i</i> concentration,	[ML ⁻³]
	in the mass balances under stagnation or flow.	
Q_X	Biomass concentration.	$[M_{X}L^{-3}]$
[<i>i</i>]	Concentration of substrate <i>i</i> .	mol/L
{ <i>i</i> }	Activity of substrate <i>i</i> .	mol/L
D	Molecular diffusion coefficient.	$[L^2T^{-1}]$
r(q)	Production/consumption rate of the substrate.	$[ML^{-3}T^{-1}]$
\hat{q}_i	Maximum rate of substrate <i>i</i> .	$[M_i M_X^{-1} T^{-1}]$
φ_i	Saturation factor of substrate <i>i</i> .	[dimensionless]
Y_i	Bacterial yield coefficient for substrate <i>i</i> .	$[M_X M_i^{-1}]$
L_f	Maximum biofilm thickness.	[L]
L_L	Thickness of the biofilm diffusion layer.	[L]
MWi	Molecular weight of species <i>i</i> .	g/mol
μ_I	Ionic force.	mol/L
Γ	Ratio between the amount of Cu complexed to the	$[M_{Cu} M_X^{-1}]$
	biomass and the amount of biomass.	
ϕ	Pipe diameter	[L]
Q _{TUB}	Flow rate that circulates through the pipe.	$[L^{3}T^{-1}]$
R	Pipe radius.	[L]
μ	Water dynamic viscosity.	$[ML^{-1}T^{-1}]$
r _c	Correlation index.	[Dimensionless]

The description of the mathematical and numerical implementation of this model, along with its processes, is presented in the following section.

2.2.1. Mass flow under stagnation

The mathematical model is based on the mass balance equation, which is numerically solved by the use of finite volumes (FV). Each FV is modeled as a completely mixed reactor. The model presented here uses two sizes of FV's, one for macroscopic scale and the other for microscopic scale.

In each FV we apply the mass balance equation:

$$\frac{\partial q}{\partial t} + \nabla \cdot \mathbf{f}(q) - r(q) = \mathbf{0}.$$
(1)

Here, *q* is the concentration $[ML^{-3}]$, $\mathbf{f}(q)$ is the mass flow rate at the control surface $[ML^{-2}T^{-1}]$, and r(q) is the production rate $[ML^{-3}T^{-1}]$, where r(q) < 0 indicates the consumption. We considered that under stagnation the mass flow on each FV is controlled by diffusion, which is ruled by Fick's law ($\mathbf{f}(q) = -D\nabla q$, where *D* is the molecular diffusion). Integrating spatially and temporarily the equation over a FV we obtain a set of equations to solve the model. The notation used is presented in Table 1, and details of the numerical implementation are available as supplementary material. There are two domains where mass balance occurs, two-dimensional Cartesian for the microscopic scales and one-dimensional in polar coordinates for the macroscopic scale.

The model in Cartesian coordinates with discrete Δx length cubes includes four neighbors control volumes: up, down, right, and left. And the model in polar coordinates assumes the concentration doesn't change when we vary the angle θ so the control volumes have two neighbors: North and South, as shown in Fig. 3. Details of the numerical implementation can be found in the supplementary material, Appendices A, B, and C.

2.2.2. Biofilm model

At a microscopic scale the biofilm grows on the inner surface of the pipe, covering some of the FV's as shown on Fig. 4 where L_L is the depth of the diffusion layer, which is at the edge of the microscopic scale. On the FV's occupied by the biofilm four processes were considered: (1) Diffusion, (2) substrate utilization, (3) bacterial growth and decay, and (4) biomass redistribution. Diffusion is controlled by Fick's Law, and was modeled with the corresponding differential equation [42].

The biomass production comes from the consumption of one or more substrates like Dissolved Oxygen (DO), carbon sources and nitrogen [30,33,43]. Our model assumed that the microorganisms are heterotrophs in an aerobic environment. Therefore the model considered DO as the electron acceptor and an organic substrate (*S*) as the electron donor and carbon source. The substrate consumption, bacterial growth and decay used in the model are summarized on the stoichiometric matrix shown in Table 3. It was assumed that the biomass concentration (Q_x) remains constant on every time step for diffusion and reaction computation.

To model the biofilm growth and decay we used a cellular automata (CA) approach. The CA are in a domain composed by a set of cells, whose state varies in time, which are controlled by a set of local rules that can be applied globally [44]. The biomass growth model was based on the utilization of a probability that relates the biomass growth with the probability a cell can reproduce in a time interval Δt [29,33].

The diffusion of the substrates on the biofilm occurs fast in comparison to the bacterial growth and decay [33], therefore these temporal scales were separated. This is accomplished by considering that after a certain number of steps in the diffusion process, a step of bacterial growth or decay occurs. Considering that a growth and lysis step occurs every *N* diffusion steps, the temporal discretization for these processes (ΔT) can be established $\Delta T = N\Delta t$. Under these conditions, the growth and lysis probabilities have a binomial distribution, where an event occurs every *N* steps [33].

The rule for growth and lysis is applied to the cells that contain biomass. Each cell in the grid has two states: a) empty or b) filled with biomass. At the same time, a new grid with empty cells, with the same geometric characteristics of the grid containing the biofilm, is created. A random number p_1 that has a uniform distribution U(0,1) is generated in each cell of the grid that contains the biofilm. If $p_1 \le p_g$, the biomass cell is duplicated, and the state of the adjacent cell in the parallel grid is changed to filled. Subsequently, a second random number p_2 with a uniform distribution U(0,1) is generated, and if $p_2 \le p_d$, the states for the

Table 2

Processes, spatial scales, and domains used by the mathematical model for MIC in pipes under flow and stagnation conditions.

Condition	Process	Sub-Process	Numerical Method	Spatial Scale	Domain
Stagnation	Biofilm Growth	Diffusion Substrate utilization Biomass growth/decay	Finite volume Probability of utilization [33]	micro	2D Cartesian
		Biomass redistribution within the biofilm	Cellular Automata		
	Speciation	Chemical equilibrium	Newton-Raphson	Micro Macro	2D Cartesian 1D Polar
	Copper ions release	Constant flux		Micro Macro	2D Cartesian 1D Polar
	Mass transport of species and substrates	Diffusion	Finite volume	Micro Macro	2D Cartesian 1D Polar
Flow		Advection		Micro Macro	2D Cylindrical



Fig. 3. Spatial domain used by the model: a) 2D domain in cylindrical coordinates discretized for Finite Volumes, and b) FV and neighboring cells in cylindrical 2D coordinates.

cell of the grid with biofilm and the adjacent cell in the parallel grid are changed to empty.

Once the growth and lysis rule is applied, the cells with biomass in the parallel grid must be distributed on the biofilm. This procedure is performed by applying the "random walk" rule, which has been widely used and tested in simulations for the diffusion of substrates and the redistribution of biomass in heterogeneous biofilm models [29,33,4] given the computational advantages of using bits as variables [45,46].

2.2.3. Mass balance under flow conditions

Under the flow conditions the velocity field inside the copper pipe produces advective and diffusive transport of the different species. This was modeled using the mass conservation law in cylindrical coordinates. It was assumed that the concentration of species doesn't vary with θ , so the model can be simplified to a bi-dimensional model as presented in the lower row of Table 2. So the each FV has 4 neighbors: up, down, left and right (North, South, West, and East; Fig. 3).

We considered that the velocity field only occurred on the z axis so mass flow is controlled mainly by advective transport. Thus, diffusion on this axis was considered negligible. On the r axis we only considered mass flow by diffusion. Thus, the mass flow is represented by Eq. (2)

$$\mathbf{f}(q) = -D\frac{\partial q}{\partial r}\mathbf{u}_r + q\mathbf{v}_Z\mathbf{u}_Z.$$
(2)

The divergence of $\mathbf{f}(q)$ has the following form:

$$\nabla \cdot \mathbf{f}(q) = \frac{1}{r} \frac{\partial}{\partial r} (r \, \mathbf{f}_r(q)) + \frac{\partial \mathbf{f}_z(q)}{\partial z}.$$
(3)

The details of the numerical scheme used are presented in Appendix D in the supplementary material.



Fig. 4. Schematic representation of the substratum (surface of the pipe), biofilm, and diffusion layer in the lattice used by the mathematical model.

2.2.4. Chemical equilibrium

Knowing the spatial distribution of different species of copper within the domain of the pipe is necessary to give better understanding of the corrosion process. Under stagnation, diffusion and speciation are the mechanisms that determine the distribution of the species within the pipe. These mechanisms were modeled independently and then were coupled. To determine the speciation we used chemical equilibrium conditions assuming each FV operates as a completely mixed reactor.

Chemical species concentration is calculated with PHREEQC geochemical software [47]. Each FV assumes the presence of three main components: (1) *chemical elements*, (2) *master species*, and (3) *solution species*. The combination of *chemical elements* forms *master species* and the *solution species* are created from the *master species* by a chemical reaction.

In chemical equilibrium, species concentration in the solution was calculated using three main rules: (1) mass conservation, (2) electroneutrality of the solution, and (3) non-ideal behavior of ions in the solution. The resulting set of equations was solved numerically using the Newton–Raphson method (see Appendix E in supplementary material).

2.2.5. Copper-biofilm concentration

The complexation between copper ions (Cu^{2+}) and the biomass is due to the anionic nature of the biofilm EPS [48]. Eq. (4) represents this phenomenon

$$Cu^{2+}Sf^2 \Leftrightarrow Sf \equiv Cu. \tag{4}$$

Where Sf^{-2} is the available quantity of complexation sites and $Sf \equiv Cu$ represents the cupric ions complexated with the biomass. Thus, complexation of copper ion into the biomass can be modeled applying a Langmuir adsorption model, which can be expressed in terms of mass by Eqs. (5) and (6)

$$\Gamma = \frac{MW_{Sf} \equiv Cu}{\rho_b} [Sf \equiv Cu]$$
⁽⁵⁾

$$\Gamma_T = \frac{MW_{S_T}}{\rho_b} [S_T]. \tag{6}$$

Table 3

Stoichiometric matrix for the dynamics of biomass used in the mathematical model for MIC.

Reaction	Qs	Q ₀₂	$Q_{\rm X}$	Rate/(mg/L/s)
Heterotrophic Growth	-1	-(1 - Y)	Y	$\hat{q} \cdot \frac{Q_s}{K_s + Q_s} \cdot \frac{Q_{02}}{K_{02} + Q_{02}} \cdot Q_X$
Decay			-1	$b \cdot Q_X$

Where: Y, yield coefficient; \hat{q} , maximum specific substrate utilization rate; Ks, half-saturation constant for substrate; K_{02} , half-saturation constant for oxygen; Q_{5} , substrate concentration; Q_{02} , oxygen concentration; Q_{X} , biomass concentration; and b, first-order biofilm mass decay rate.

Where Γ is the ratio between the complexed mass of copper and the biomass (M/M), Γ_T is the ratio between the total available sites and the quantity of biomass (M/M), $MW_{Sf \equiv Cu}$ is the molecular weight of the complex Cu-Biomass (g/mol), and MW_{ST} is the molecular weight of the total available sites for complexation (g/mol), and ρ_b is the density of the biomass (M/L³). The Langmuir model assumes complexation occurs in a 1:1 way, each complexed copper molecule corresponds to a single biomass site. Therefore the molecular weight of the complex Cu-Biomass (Sf $\equiv Cu$) and of the available sites (Sf⁻²) is equivalent to the molecular weight of the copper ion. Considering this, and combining Eqs. (5) and (6) we obtain Eq. (7)

$$\Gamma = \Gamma_T \cdot \frac{Q_{Cu^{+2}}}{1 + K_{eq,m} Q_{Cu^{+2}}}.$$
(7)

Where $K_{eq,m}$ is the adsorption constant expressed in terms of the mass. Eq. (7) allows for the parameters of the complexation model, the equilibrium constant *K*, and the total amount of available sites $[S_T]$ to be experimentally determined. However, the number of cupric ions complexed to the biomass is calculated by incorporating reaction (5) with the thermodynamic equilibrium model.

2.2.6. Multi-scale coupling in the mathematical model

During corrosion, the physical-chemical processes related to the presence of the biofilm occur at a microscopic spatial scale (metalliquid interface), where the Cu ions are released. Subsequently, these ions interact on the macroscopic spatial scale of the pipe domain (i.e. bulk water). Consequently, the coupling of these two scales in the mathematical model is critical to determine the influence of the processes that occur at a microscopic level on the transport and release of copper at a macroscopic level and, in this way, to better understand the MIC phenomenon in copper pipes.

The microscopic scale is modeled using a Cartesian two-dimensional domain where the biofilm growth, the release of Cu ions, the diffusive transport of the chemical species, and the speciation occur. In contrast, the macroscopic scale is modeled using a polar one-dimensional domain where the chemical speciation and the diffusive and advective transport of species occur. These spatial scales are shown schematically in Fig. 5. From the mathematical point of view, these spatial scales are coupled by assuming that the concentration of the chemical species at



Fig. 6. Variation of dissolved copper, temperature, and pH as a function of the volume extracted from the experimental pipe. Data represent the results from 10 days of sampling at field experiments. Error bars represent maximum and minimum values measured.

the upper boundary of the two-dimensional domain does not vary along the *x*-axis, that is:

$$\left. \frac{\partial q}{\partial x} \right|_{y=Lf+L_L} = 0 \tag{8}$$



Fig. 5. Coupling of the spatial scales in the mathematical model for corrosion in copper pipes. The coupling states that the concentration of the FV of the 2D domain located at the interface with the FV of the 1D domain, do not change along the *x* axis.

Table 4

Parameters for temporal and spatial discretization used in the mathematical model to generate biofilm structures.

Parameter	Symbol	Unit	Value
Spatial discretization	Δx	μm	5
Domain Length	L _x	μm	1000
Domain Height	L_{v}	μm	500
Number of rows	Ň _x	-	100
Number of columns	N_y	-	200
Temporal discretization	Δt	min	0.1
Temporal discretization for biomass growth	ΔT	min	60
Simulation time	Т	d	365
Number of steps to compute	N_p	-	5.256×10^{3}
Number of steps for biomass growth	N _c	-	600

In this way, the discretized mass balance equations during the stagnation conditions in the cells n_rad of the one-dimensional domain (macroscopic) and n_row of the two-dimensional domain (microscopic) as shown on Fig. 5 take the following form:

Row n_rad:

$$a_{S}Q_{n_rad-1}^{n+1} + a_{P}Q_{n_rad}^{n+1} + a_{N}Q_{n_row}^{1D,n+1} = b_{1,n_rad}.$$
(8)

Row n_row:

$$a_{S}Q_{n_rad}^{n+1} + a_{P}Q_{n_row}^{1D,n+1} + a_{N}Q_{n_row-1}^{1D,n+1} = b_{1,n_row}.$$
(9)

Where:

$$Q_{n_row}^{1D,n+1} = Q_{n_row,j}^{n+1} \forall j = 1, ..., n_col$$
(10)

$$Q_{n_row-1}^{1D,n+1} = \frac{1}{n_col} \sum_{j=1}^{n_col} Q_{n_row-1,j}^{n+1}.$$
 (11)

The coefficients a_S , a_P , a_N and b_1 are computed for the discretization used and are a function of the time step, FV size, and diffusion coefficient (see Appendix B in the supplementary material).

In the microscopic domain the cells are on the order of microns, whereas in the macroscopic domain the cells are on the order millimeters, this is a difference of three orders of magnitude. This situation causes problems in the convergence of the numeric scheme of the FV's, especially in the cells that are on the edge of the coupling. To address this situation, a transition zone was created, where the size of the cells varies from Δx (size of the 2D Cartesian domain cells) to Δr (size of the 1D polar domain cells). To implement this solution we used a transition parameter (f_T), which changes the size of the cells in a linear fashion.

2.3. Model validation

The mathematical model was validated using experimental data obtained from an actual pipe systems affected by MIC. The system consisted of a well connected to a PVC pipe followed by a 1 m long copper pipe of internal radius of 1.95 cm (3/4 inch). Before the study was performed the system was in operation for 2 years under domestic conditions. The system was kept in a state of stagnation for 10 h before the application of a flow, which had a constant rate of 0.48 L/min (Re = 587) [40]. Each day, for 10 consecutive days, 15 samples were collected at different times during the flow experiment. Dissolved and total copper concentrations were measured in-situ by the bicinchoninate method (HACH #8506) with a portable spectrophotometer HACH DR/2010 [49]. The concentration of copper for each sample was measured and copper release curves were obtained. Dissolved copper was measured after membrane filtration (0.45 µm pore size cellulose acetate) and total copper was quantified in unfiltered samples after acidification with nitric acid [40]. The summary of the results of the field data is presented in Fig. 6. It can be observed that the concentration of copper in the water decreases as the volume of water that exits the pipe increases. The average mass of copper released during the experiment (integral under the curves in Fig. 6) was 10.3 mg, approximately 11 times the mass of copper expected considering ideal plug flow within the pipe (the product of the dissolved copper within the pipe - initial Cu concentration - and its volume), suggesting



Fig. 7. Average biofilm thickness over time obtained with the mathematical model (upper panel). A representative structure for lower, average and maximum biofilm thickness was selected for days 198 (Structure 1.1), 214 (Structure 1.2), and 238 (Structure 1.3). The Structure 1.3 (thick biofilm) is shown in the lower panel.

that there is an enhanced release of copper, probably due to biomass adsorption/desorption of copper ions.

The average total mass of copper released during flushing experiments was 10.3 mg, 11 times the mass of copper predicted with the traditional ideal plug flow assumption.

The physicochemical parameters required by the mathematical corrosion model were obtained from experimental data and the literature. These parameters included speciation chemical reactions and thermodynamic constants [47,50], diffusion coefficients and molecular weight of chemical species and substrates [51,52], Cu-Biomass complexation constants [53], physical properties of water [54,55], and biofilm kinetic and metabolic parameters [52,56,57].

3. Results and discussion

The main physicochemical parameters that define the copper release are the heterogeneous biofilm structure, the mass flow of copper ions under stagnation ($J_{Cu^{+2}}$), the ratio between the copper diffusion coefficient inside the biofilm and the liquid (D_f/D_L Cu²⁺), the total quantity of available sites for the copper-biomass complexation (S_T) , the logarithm of the constant equilibrium of the copper biomass concentration (Log K), and the flow within the pipe.

The model was compared to the experimental results using biofilm structures generated for the conditions measured in the field. We used a concentration of organic carbon of 1.5 mg/L to support biofilm growth, kinetic parameters from the literature for heterotrophic bacteria, and the discretization parameters shown in Table 4. From the simulation of the biofilm structure over time, 3 representative structures were selected, considering the stages on which the biofilm thickness was minimum (Structure 1.1), average (Structure 1.2) and maximum (Structure 1.3). These structures correspond to days 198, 214 and 238 respectively, and are presented in Fig. 7.

With these biofilm structures the mass flow of the copper ions $(J_{Cu^{+2}})$ during stagnation was calibrated. This was done adjusting the model to the copper release curve observed on the experiments using minimum square fitting. During the stagnation the biofilm structures were considered static because in 10 h the changes on the biofilm structure are insignificant. This can also be verified in the simulation of thickness over



Fig. 8. Simulation of spatial distribution of dissolved copper + complexed copper in biomass at the microscopic scale after stagnation time (10 h) for the Structures selected.

time in Fig. 7, where significant changes of biofilm thickness occur in the lapse of days. On the other hand, during flow conditions we assumed that the copper sorbed on the biomass was released instantaneously. The results of the simulation after stagnation are presented in Fig. 8.

The results from the experiments of flow under laminar conditions and with the presence of a biofilm show that the release of copper decreases as the volume of water flowing through the pipe increases (Fig. 6). Computing the mass of copper released it is possible to verify that this mass is greater than the mass estimated using only the concentration of copper of the bulk water within the pipe and the volume of the pipe [40]. Fig. 9 presents the results of copper release under flow conditions for the three biofilm structures simulated. The panels at the left side are longitudinal cross sections of the pipe, indicating the concentration of copper after the stagnation condition. It can be observed that most of the copper is associated to the biomass which is attached to the inner surface of the pipe. The right panels indicate the copper release curve for the numerical experiments for the three biofilm structures presented in Fig. 8. The best fit resulted for structures 1.2 and 1.3, which correspond to thicker biofilms. The model results demonstrate that the Cu-biomass complexation is relevant when there is a biotic layer on the pipe walls (biofilm). This is also in agreement with the results presented by Calle el al. 2007. Nevertheless, only a 3% of the maximum complexation capacity of the biomass (52.75 mg Cu/g cells) was reached after the 10 h of stagnation. This suggests that the reactive surface can act as a copper reservoir, which can be released by hydrodynamic mechanisms during flow. When comparing experimental results from pipes without a mature biofilm and the data from the field and modeling, we observe that diffusion transport is not the main mechanism that governs copper release when there is a reactive surface, such as the biofilm. Instead, the results of the model suggest that complexation of Cu-Biomass and hydrodynamics mechanisms are the most important factors for copper release into the water.

Our model assumed that copper release from the biomass under the flow condition occurred instantaneously. This kinetic is probably related to the shear stress produced by the velocity field, but uncertainty exists about how these mechanisms operate in the reactive surface, and studies are still needed for further understanding.



Fig. 9. Left panels: dissolved and biomass-complexated copper profile within the pipe after stagnation time. Right panels: copper release curves observed (Box–Whisker) and simulated (line) for (a) Biofilm structure 1.1, (b) Biofilm structure 1.2, and (c) Biofilm structure 1.3.

The adjusted copper mass flux of the field experiment $(J_{Cu^{+2}})$ was 3.88×10^{-6} mg Cu cm⁻² min⁻¹. Uniform corrosion rates reported in the literature under different conditions can be translated into a constant mass flux. Edwards and Ferguson [58] studied the corrosion of coupons artificially aged obtaining corrosion rates for an equivalent age of 210 days. These rates varied from 1.59×10^{-5} mg Cu cm⁻² min⁻¹ for pH = 6.8 to 3.10×10^{-5} mg Cu cm⁻² min⁻¹ for pH = 9.3. Zhang et al. [59] reports the corrosion rates for stagnation periods of 2 to 30 days. Their results showed that corrosion rates stabilize after 8 days and has a value of 1.70×10^{-7} mg Cu cm⁻² min⁻¹ for pH = 8. Finally, Broo et al. [60] reported corrosion rates of 3.39×10^{-5} mg Cu cm⁻ min^{-1} in copper coupons after 8 h of stagnation at pH = 6.4 and alkalinity of 6 mg CaCO₃/L. The values estimated by our model are within the reported values of the literature and an order of magnitude higher than typical values for pipes without the presence of biofilm. This demonstrates the importance of biofilm presence on copper release during stagnation.

4. Conclusions

This research has developed a complex mathematical model for predicting the corrosion rate and copper release in copper drinking water distribution systems. We have been able to reproduce the relevant mechanisms that influence copper release into drinking water systems subject to stagnation and flow cycles when there is a biofilm covering the inner surface of the pipe. We have modeled and integrated the interaction of physicochemical processes that occur at microscopic and macroscopic scales.

Copper release curves can be accurately reproduced when the model reproduces the interaction with the reactive surface of the pipe once flow within it establishes. This was reported by Calle et al. [40] as a conceptual model. Our model integrated the biofilm structure and properties to a hydrodynamic model, thus stating the importance of biofilm EPS in the complexation of copper ions during stagnation and further release during flow conditions due to shear stress.

The model also reproduces the spatial heterogeneity observed in actual biofilms growing on the surface of copper pipes [40]. This heterogeneity may provide the conditions to form micro-electrochemical cells on the surface of the metal, inducing the release of copper ions during stagnation.

This research is a first step to include the hydrodynamic mechanisms on copper release on household pipes subject to MIC. However, there are still aspects that require further research and could be incorporated to provide a better understanding and prediction of copper release. These include: i) Considering the electrochemical parameter on the copper release from the pipe walls, using kinetics such as Butler-Volmer. These would provide a better understanding of the electrochemical microcells on the surface of the wall; ii) Including the effects of the corrosion solid by-products, considering the release of copper due to dissolution or detachment of nano particles produced by shear stress. This would allow quantifying the contribution of solid products on copper release; iii) Establishing a kinetic model for the released of copper sorbed to the biomass under the flow conditions, relating the shear stress and concentration gradient with the copper release. These would allow a better understanding of the biofilm as a copper ions reservoir; and iv) Improving the turbulence effect by the introduction of a small random speed normal to the longitudinal axis of the pipe. These would allow a better simulation of the hydrodynamic mechanisms.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx. doi.org/10.1016/j.bioelechem.2013.12.004.

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