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Modelling drinking water chlorination at the Breakpoint: II. Calculation of the chlorine and chloramine concentrations along municipal pipe

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ABSTRACT

This study is focused on the determination of added chlorine dose in low ammoniacal concentration contained in distribution pipe of drinking water. The chlorine concentration in disinfected water varies between events of lack and excess that must be regularly controlled. The chlorine transport from the inlet to the outlet of pipe is carried out in turbulent flow where the phenomena of diffusion and convection are in charge to convey chlorine and chloramines formed along the polyvinylchloride pipe. The chlorine decay is principally due to ammonia consumption in the water bulk. The chlorine demand serves to generate inorganic chloramines and the formation of an uncertain intermediate, which helps to destruct them, and the reactions series of formation-destruction are referring to Breakpoint chlorination. The set of presented reactions at Breakpoint chlorination are not clear and the observed rate constants are not similar in the researchers found in the literature. Then, their choices are not easy because they cause large differences between the experimental profiles of disinfectants concentrations taken from literature and the predicted profiles of disinfectant concentrations investigated in the present paper. The set of differential equations are resolved simultaneously by the method of finite differences. Therefore the concentrations of free residual chlorine, ammonia, monochloramine, dichloramine, trichloramine, nitrogen hydroxide and total chlorine are calculated at different points constituted the municipal pipe.

Keywords: Chlorination; Bulk decay; Observed rate constants; Modelling; Equation transports

1. Introduction

The control and the monitor of chlorine dose and chloramine concentrations during the flow of drinking water released from the treatment plant to a consumer through a distribution pipe requires an achieve of two main purposes: research of present species or the set of reactions at breakpoint chlorination and a transport model. These data allow forecasting the necessary amounts of chlorine and chloramines for disinfection. Therefore, this way of proceeding with the free chlorine residual and the chloramine concentrations becomes efficient. Namely, where there is a lack in chlorine we should add a specified quantity of solid or liquid chlorine necessary to Breakpoint dose for ensuring the water disinfection and where there is an exceeded dose of chlorine we can reduce an amount

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of chlorine to prevent the water contamination against corrosion products, biomass proliferation and byproducts formation.

The treatment of drinking water remains always: a sanitary, an economical, an environmental, a political, and a cultural worry for the scientists and the governments. The disinfection step is especially critical. Although in previous century, the disinfection technology development reported that approximately 20–40% of urban water systems in developing world their water supply were not disinfectant [1].

Chlorine is very useful for water disinfection uses because it is stable to maintain a microbiology quality by reducing the bacteria proliferation in the storage tanks and distribution network pipes [2]. However it is very necessary to precise that when we disinfect water with chlorine, so this water should be devoid of organic materials. In other hand the chlorination is very benefic when the AOC is less than 50 μg/l for limiting the bacteria growth [3]. Other researches had observed that an overdose of chlorine leads to accelerate the bacteria proliferation high than 1.9×10^4 bacteria per cm^2 in the presence of 1–2 mg/l of free chlorine residual [4]. For this reason it is very important to assess precisely the chlorine dose that is necessary to add at reservoir stocks and network pipes. The chlorine dose required to disinfection should make compromise between microbial risks and chemical risks, in other words this chlorine dose should be sufficient for destroy organisms causing disease of drinking water and does not produce chlorination by-products CBPs and deposits products like the appearance of corrosion layers and/or biofilms that are harmful for the human health [5–7]. Moreover, the inactivation of microorganisms by disinfectants follows several equations proposed in literature [8].

The main objective of this paper is to predict models of bulk decay for chlorine and chloramines at Breakpoint chlorination in low ammoniacal water flowing in municipal pipe in order to find concentrations of chlorine and chloramines on all points of pipe axis. Then, we compare our predicted results with the experimental results of Lu et al. [9]. For reasons of comparison, this modelling investigation must use their experimental conditions. In this instance, the review of several works on the chlorine decay seems important on the one hand, it allows to validate the suppression of such chlorine rate constants or omitting some terms vs. others, on the other hand we distinguish the different models studied in literature of chlorine transport in distribution pipes or network in different assumptions to deduce the best results. Hallam et al. [10] studied the chlorine consumption at pipe wall; study by Rossman et al. [11] focused on chlorine decay in metallic pipes. Moreover, the impact of chlorine on fixed biomass or biofilms has been investigated by Pedersen [12], Dahi [13], Lu et al. [14], Niquette et al. [15], Batté et al. [16] and Tsvetanova [17]. The chlorine rate coefficient in the water bulk has been also estimated in work's Jonkergouw et al. [18]. Then, the influence of pipe material, water quality and the hydraulic effects on combined chlorine have been underlined by Mutoti et al. [19]. In addition, the influence of the initial concentration of chlorine C0 and the temperature on the bulk decay had been carried out by Hua et al. [20]. Furthermore, the chlorine transport has been modeled and/or simulated in several rehearses in outfit operatory conditions and assumptions, like works of Lu et al. [9,21], Biswas et al. [22], also for Osman et al. [23,24], Muslim et al. [25], Hua et al. [20], Munavalli and Kumar [26], Cozzolino et al. [27], Jadas-Hécart et al. [28], Dossier-Berne et al. [29] and Rossman et al. [30]. These models are proposed in different flow types (laminar, turbulent and plug) with diffusion or convection or both phenomena in stationary or non-stationary steady state, in the wall pipe and/or bulk pipe, also these models are proposed only for chlorine transport or with the combined chlorine or total chlorine where the difference between the free residual chlorine and the combined chlorine is in the mass transfer coefficients and observed rate constants that are linked to temperature and pH, the evaluation of these constants do not agree with the research by Wei and Morris [31], Selleck and Saunier [31], Morris and Issac [32], and Qiang and Adams [33].

Some models are resolved by analytical solutions and other by numerical solutions followed by programming language or by using ready software like Epanet-MSX [34,35] designed for forecasting chlorine dose where the pipe material, pipe age, pipe dimensions, flow regimes, the physico-chemical parameters of water are entered as data. However, we have obtained our results by a numerical method followed by establishment a program in Fortran 95 in order to find the concentration of chlorine and its derivatives along the distribution pipe for the system control.

2. Transport equation

The assumptions used when the addition of chlorine to ammoniacal water flowing in a pipe during disinfection at breakpoint chlorination are expressed as:

(a) The work in diluted aqueous solution permits to use concentration instead of activity because the activity coefficient is equal to unit. Besides, the ammonia concentration is around 1 mg/l, and the process of chlorine dosage is carried out far from the inlet of pipe, then the chlorine and ammonia are well mixing and hence form a homogenous solution.

(b) All charged species are not taken into account in following equations like Cl^-, NO_3^-, etc.
(c) There is no change in temperature (an isothermal process).
(d) Water flows in a new material of polyvinylchloride (PVC) pipe which is unreactive with chlorine and combined chlorine that is to say there is not formation of biomass or corrosion layers on the pipe wall. Then, the wall consumption of chlorine can be neglected comparing to the bulk consumption [10], and due to the presence of ammonia in the bulk water, the detail of this study will be viewed after. The Fig. 1 shows the case of study.
(e) Pipe dimensions, the length 13,200 cm and the diameter 1.9 cm [9], here it is necessary to note that the ratio surface to volume is equal to 2.1, this improves the neglect of the wall reactions with chlorine [14].
(f) The values of parameter flow are: the flow rate $120\,cm^3\,s^{-1}$ and average velocity $42.3\,cm\,s^{-1}$, the Reynolds number Re results from this data is equal to 8,013 at 20°C greater than 4,000, then the flow nature is turbulent [36].

The overall equation of transport is in a function of cylinder coordinates where the transfer phenomena of diffusion, convection and chemical transformations of chlorine are responsible to: vehicle and consume chlorine species between the inlet to the outlet of pipe [37]:

$$\Delta_t C + U(x, r, \theta)\Delta x\ C = \Delta r\ \Delta x(DC) - R_k(C, t) \tag{1}$$

Here, there is not rotation around the angle θ, and the expression of Eq. (1) in the form of developed derivative without θ is a function of r and x coordinates, is given thus:

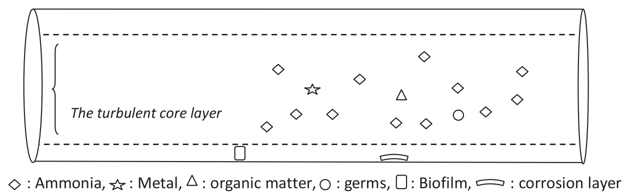

Fig. 1. Simplificated chlorine reactions in bulk and wall of pipe.

$$\frac{\partial C}{\partial t} + U\frac{\partial C}{\partial x} = D_L\frac{\partial^2 C}{\partial x^2} + \frac{D_r}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C}{\partial r}\right) - R_k(C, t) \tag{2}$$

The first term on the left represents the accumulation of species with time; the second term shows the axial convection. The first and the second terms on the right are the radial and the longitudinal diffusion, respectively and the last term is the chemical reactions [22,23]. The simplified equation of transport can be written in steady-state with neglect of the axial diffusion due to the evaluation of the axial Péclet number Pe_a that is found greater than 10^6 which allows the neglect of the longitudinal diffusion term compared to the convection term. However, the radial Péclet number Pe_r shows that the convection radial member cannot be neglected compared with the radial diffusion term. Therefore, the equation is expressed according to [9,22]:

$$U\frac{\partial C}{\partial x} = \frac{1}{r}\frac{\partial}{\partial r}\left(rD_r\frac{\partial C}{\partial r}\right) - R_k(C) \tag{3}$$

where U is the local velocity profile which depends on the flow behavior obtained by the mean of velocity distribution [38], this latter is expressed according to the turbulent flow. Then, the local velocity is defined as:

$$U = v \times f(r) \tag{4}$$

where v is the average velocity and $f(r)$ is the flow parameter, it depends on the flow regime that is to say on the Reynolds number Re and the radial position r. For the laminar flow $f(r) = 2\ [1 - (\frac{r}{r_0})^2]$, and when the plug flow accounting $f(r)$ is equal to 1 [9,22]. But in the turbulent regime, the flow parameter has as expression Eq. (5) when the Reynolds number Re is between 2,300 and 30,000 [23,24]. Moreover, there are other expressions of velocity profiles for turbulent core [14,39] that are not presented here, In our study Eq. (5) has given best results according to our knowledge.

$$f(r) = \sqrt{(f)}\left[\left(2.15\log\frac{r_0 - r}{r_0} + 1.43\right)\right] + 1 \tag{5}$$

Besides, the position where $r = 0$, the velocity flow is maximal and it is referred to the central velocity v_c which is the ratio of central velocity to average velocity, the ratio is expressed by Eq. (6). In this way, the maximal velocity does not differ much from the average velocity which is the feature of turbulent regime profile.

$$\frac{v_c}{v} = 1.43\sqrt{f} + 1 \tag{6}$$

The value of Reynolds number Re is previously calculated 8013 at 20°C including in turbulent flow regime as well as the PVC pipe is characterized by smooth walls that permits to use friction factor data of BLASIUS for Reynolds number Re range 3,000–100,000 calculated by using Blasius formula [40]:

$$F = \frac{1.316}{R_e^{0.25}} \tag{7}$$

As regards the diffusivity coefficient D, it is rather to remember that generally, a fluid is divided into three layers: the thin sublaminar layer adjacent to the wall, the turbulent core, and the buffer region between the core and laminar layer [41] as illustrated in Fig. 2. Besides, the chlorine reactions are taken place in the turbulent core layer where the value of the mass diffusivity is larger than the molecular diffusivity in the turbulent core (Fig. 2). Indeed, the mass transfer coefficient was computed using the diffusivity of chlorine $1.44 \times 10^{-5}\,\text{cm}^2\,\text{s}^{-1}$, assumed to be equal to that for chloramines [19]. To expand and clarify, the range of magnitude between the eddy diffusivity and molecular diffusivity let take chlorine values $D_{\text{eddy}} = 40\ \text{cm}^2\,\text{s}^{-1}$ and $D_{\text{mol}} = 5 \times 10^{-9}\text{cm}^2\,\text{s}^{-1}$, respectively [27]. Moreover, the use of the relationship $D_{\text{eddy}} = 1.233 \times 10^{-2} \times v \times d$ gives the eddy diffusivity follow $0.495\,\text{cm}^2\,\text{s}^{-1}$ [9,21,22] and the other expression of the eddy diffusivity is illustrated by Eq. (9) gives $0.298\,\text{cm}^2\,\text{s}^{-1}$[23,24]. The best result is given by the formula which represents the smallest eddy coefficient.

$$D = D_{\text{eddy}} + D_{\text{mol}} \tag{8}$$

$$D_{\text{eddy}} = 0.02 \times v \times d \times f^{0.5} \tag{9}$$

Concerning the diffusivity values of eddy and molecular, those of chlorine are $2.98 \times 10^{-1}\text{cm}^2\,\text{s}^{-1}$ and $1.25 \times 10^{-5}\text{cm}^2\,\text{s}^{-1}$, respectively [9]. Consequently, we deduce that the eddy diffusivity is greater than the molecular diffusivity and so the D_{mol} can be neglected with respect to the D_{eddy} and then $D = D_{\text{eddy}}$.

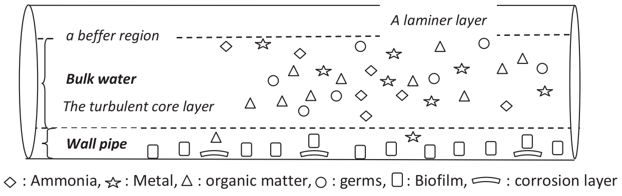

Fig. 2. Chlorine reactions in bulk and wall of pipe.

The expression members of transport equation are precisely chosen from reviewed works found on the chlorine decay in the network distribution studies but applied in the already mentioned assumptions; we can reach to the final equation follow:

$$V\left(\sqrt{f}\left[\left(2.15\log\frac{r_0 - r}{r_0} + 1.43\right)\right] + 1\right)\frac{\partial C_k}{\partial x} = D^2\frac{\partial C_k}{\partial r^2} + \frac{D}{r}\frac{\partial C_k}{\partial r} + R_k(C) \tag{10}$$

where $R_k(C)$ presents the kinetics of chemistry reactions of species k that is expressed in the transport equations below.

3. Chlorine consumptions

The addition of chlorine to ammoniacal water contained in network pipes produces generally several reactions of chlorine with different substances included in water. These reactions are referred to the chlorine demand that includes two types of chlorine consumption: the bulk chlorine decay and the wall chlorine decay.

- The bulk chlorine decay is affected by temperature, the initial chlorine concentration, and the organic matter content in the water [42], the results reveal that the bulk decay constant is proportional to the reciprocal of the initial chlorine concentration, it exists also an exponential relationship between the temperature and the initial chlorine concentration and the decay rate [20]. So the bulk chlorine decay includes the chlorine reactions:

(a) With water: When chlorine is added to the water as gas, this later is dissolved in water to form a homogenous aqueous phase, this equilibrium can be expressed by HENRY's law [43]. Then the reactions of hydrolysis and ionization of chlorine take place [44], ammonia is also subject to hydrolysis and ionization reactions, the Table 1 summarizes the reactions of hydrolysis and ionization of chlorine and ammonia in water.

(b) With inorganic compounds: Chlorine oxidizes inorganic substances such as hydrogen sulfide (H_2S), iron (Fe^{2+}), and manganese (Mn^{2+}), etc. [50–53].

(c) With ammonia: This part is the object of the first part of last paper. Although, one remembers briefly that chlorine reacts with ammonia to yield a series of chlorinated ammonia compounds named chloramines [50,51,54], followed by the destruction of combined

Table 1
Reactions of hydrolysis and ionization of chlorine and ammonia in water

Reactions	Thermodynamic constants at 25℃	References
$Cl_{2(g)} \leftrightarrow Cl_{2\ (aq)}$	$K_{HCl} = 6.00 \times 10^{-2}$ M atm^{-1}	[45]
$Cl_{2(aq)} + H_2O \leftrightarrow HOCl + H^+ + Cl^-$	$K = 3.94 \times 10^{-4}$	[46]
$HOCl \leftrightarrow OCl^- + H^+$	$K_{a1} = 2.90 \times 10^{-8}$	[47]
$NH_{3(g)} \leftrightarrow NH_{3(aq)}$	$K_{HN} = 6.61 \times 10^{-2}$ M atm^{-1}	[48]
$NH_4^+ \leftrightarrow NH_{3(aq)} + H^+$	$K_{a2} = 5.649 \times 10^{-10}$	[49]

chlorine producing the formation of the free chlorine residual necessary to protection against degradation of water quality due to microbiological growths, these equilibriums of formation–destruction of chloramines are referred to reactions of Breakpoint chlorination, which are depicted in Table 2. Incidentally, this subject is a controversy, it appears in the literature a disagreement on the reactions which are present at breakpoint reactions [31,32] and the determination of intermediate formula is not agree in research works, nitrogen hydroxide NOH appears in works [31,50] and the dichloro-nitrogen anion NCl_2^- or hydroxylamine NH_2OH [55]. Breakpoint reactions are running by several factors: pH, the initial molar ratio, temperature and the contact time [56–59]. Table 3 reports the Arrhenius expressions in which the temperature factor appears important in the stability of species, and Table 4 shows the link of pH parameter in the distribution of generated species. The overall reaction for breakpoint is [50]:

$$2NH_2Cl + HOCl \rightarrow N_2 + 3HCl + H_2O \tag{11}$$

(d) With organic substance: Chlorine reacts with humic substances to form chlorination by-products like THMs, HAAs and other CBPs, these reactions are favored at high pH and in the presence of excess of initial chlorine concentration [60]. So the chlorine dose is in competition between ammonia and organic substances owing to the neighborhood of formation constants 10^6 and 10^7 M^{-1} S^{-1}, respectively [61], in particular in small quantity of humic substances compared with ammonia amount which favors to the formation of chloramine [62,63] and chloramine may give amine nitrogen [64] or leads to its decomposition [65].

Table 2
The model of Breakpoint reactions

$HOCl + NH_4{}^+ \rightarrow NH_2Cl + H_2O + H^+$	(1)
$HOCl + NH_2Cl \rightarrow NHCl_2 + H_2O$	(2)
$HOCl + NHCl_2 \rightarrow NCl_3 + H_2O$	(3)
$NCl_3 + H_2O \rightarrow HOCl + NHCl_2$	(4)
$NHCl_2 + H_2O \rightarrow NOH + 2H^+ + 2Cl^-$	(5)
$NOH + NH_2Cl \rightarrow N_2 + H_2O + H^+ + Cl^-$	(6)
$NOH + NHCl_2 \rightarrow N_2 + HOCl + H^+ + Cl^-$	(7)

(e) With germs: The successful of disinfection with chlorine is evaluated by the change in concentrations of indicator organisms. There are some investigations on the inactivation kinetics of bacteria in the presence of chlorine as the Collins model predicts, the reduction of bacterial concentration as a function of chlorine residual concentration and contact time as $Y_t = Y_0(1 + 0.23Ct)^{-3}$ [66], and $N = N_0(1 + kC_0t)^{-\lambda/k}e^{\mu t}$, the bacterial inactivation rate follows kinetics law of first order with respect to the bacterial density where the rate constant for free chlorine k is equal to 114 lg^{-1} h^{-1},and the inactivation rate constant is $\lambda = 3.06 \times 10^4$ lg^{-1} h^{-1} [13].

- Chlorine wall decay is affected by the nature of pipe material as well as the rate of chlorine transport [11], this is confirmed by relationship existed between flow velocity and wall decay for all pipe surveyed sections [10].

Table 3
Arrhenius expressions

	Expressions of kinetics constants	References
(1)	$K_{c1} = 5.40 \times 10^9$ exp $(-2{,}237/T)$	[33]
(2)	$K_{c2} = 3.00 \times 10^5$ exp $(-2010/T)$	[32]
(3)	$K_{c3} = 2.00 \times 10^5$ exp $(-3{,}420/T)$	[32]
(4)	$K_{c4} = 5.10 \times 10^3$ exp $(-5{,}530/T)$	[32]
(5)	$K_{c5} = 2.11 \times 10^{10}$ exp $(-3{,}623/T)$	[31]
(6)	$K_{c6} = 5.53 \times 10^7$exp $(-3{,}020/T)$	[31]
(7)	$K_{c7} = 6.02 \times 10^8$ exp $(-3{,}020/T)$	[31]

Table 4
Observed rate constants

Constants	Expressions	References
K_{o1}	$\frac{K_{c1}}{[(1+K_{a1}/[H^+])(1+k_{a2}/[H^+])]}$	[31]
K_{o2}	$\frac{K_{c2}}{\left(1+\frac{K_{a1}}{[H^+]}\right)}$	[31]
K_{o3}	$\frac{K_{c3}}{\left(1+\frac{K_{a1}}{[H^+]}\right)}$	[31]
K_{o4}	k_{c4} [H$^+$]	[31]
K_{o5}	K_{c5} [OH$^-$]	[55]
K_{o6}	k_{c6}	[31]
K_{o7}	k_{c7}	[31]

The majority of researches have been carried out using the first-order decay rate equation and the factors which have been shown the influence on the wall decay are: the pipe material and the diameter, the initial chlorine concentration, the corrosion and the biofilm [10]. Unfortunately, it never exists a material pipe that will completely protect the water from changes in alkalinity, in pH or both for a long period, caused by redox, hydrolysis, and complexation or precipitation reactions of inorganic, organic or biological nature [67].

(a) With biofilm: Biofilms are formed on different materials expressing by bacterial density [17] that vary with diffusion phenomenon and velocity flow [68]. Furthermore, lower water temperatures inhibit the biofilm activity which can be counted by a relationship combining the chlorine concentration and temperature [69]. Indeed Niquette et al. [15] found the densities of bacterial biomass fixed on plastic-based pipe materials were lower than cement-based pipe materials. Wall reaction constants related to unlined ductile iron pipe for free chlorine are first order ranged from $1.27–5.32 \times 10^{-5}\,\mathrm{s}^{-1}$ depending on chlorine dose and the nature of treated water [11]. Furthermore, biomass chlorine demand is related to the pipe diameter, which means that the smallest diameter of pipe is the highest for the chlorine demand will increase [14]. Other works have evaluated the chlorine wall consumption in PVC pipes, they found that the constant decay at wall pipe in order of degree $10^{-7}\,\mathrm{m\,s}^{-1}$ this wall consumption is due to the reaction of chlorine with biomass formed on the wall pipe [22].

(b) With material pipe: Metal ions were shown to accumulate within the biofilm is possibly from the metal itself, particularly which of molybdenum, nickel, chromium and iron, which reached quite high concentrations in the biofilm of stainless steel [70].

Another case is usually presented; some bacteria and particulates can exist in both the bulk and surface phases and transfer from one phase to another by such mechanisms as physical attachment/detachment, chemical adsorption, or molecular diffusion [35].

The simplest model to describe chlorine decay uses first-order decay with respect to chlorine [71].

$$\frac{\mathrm{d}c}{\mathrm{d}t} = -k_{\mathrm{total}}C \tag{12}$$

Therefore the overall decay constant is defined as the sum of the constants of bulk and wall:

$$K_{\mathrm{total}} = k_w + k_b \tag{13}$$

$$\frac{\mathrm{d}c}{\mathrm{d}t} = -(k_w + k_b)C \tag{14}$$

Chlorine disappears in water distribution due to concurrent reactions with multitude of aqueous constituents in bulk, if it is assumed that chlorine disappears in the bulk of the water due to n reactions that are first order with respect to both reactants and second order overall, the rate of the decay of chlorine is described by [18]:

$$\frac{\mathrm{d}C_t}{\mathrm{d}t} = -C_t \sum_{i=1}^{n} K_i X_{i,t} \tag{15}$$

with $X_{i,t}$ is the concentration of the ith aqueous species at time t that reacts with chlorine with rate constant K_i

- Transport expressions
  (1) Hypochlorous acid C1:

$$v\left(\sqrt{f}\left[\left(2.15\ \log\frac{r_0 - r}{r_0} + 1.43\right)\right] + 1\right)\frac{\partial C_1}{\partial x} = D\frac{\partial^2 C_1}{\partial r^2} + \frac{D}{r}\frac{\partial C_1}{\partial r} - k_{o1}C1C2 - k_{o2}C3C1 - k_{o3}C4C1 + k_{o4}C5 + k_{o7}C6C4 - k_{\mathrm{total1}}C1 \tag{16}$$

(2) Ammonia $C2$:

$$v\left(\sqrt{f}\left[\left(2.15\ \log\frac{r_0-r}{r_0}+1.43\right)\right]+1\right)\frac{\partial C_2}{\partial x}$$
$$=D\frac{\partial^2 C_2}{\partial \mathrm{r}^2}+\frac{D\partial C_2}{r\ \partial \mathrm{r}}-k_{o1}C1C2-k_{\mathrm{total}}C2 \tag{17}$$

(3) The monochloramine $C3$:

$$v\left(\sqrt{f}\left[\left(2.15\ \log\frac{r_0-r}{r_0}+1.43\right)\right]+1\right)\frac{\partial C_3}{\partial x}$$
$$=D\frac{\partial^2 C_3}{\partial \mathrm{r}^2}+\frac{D\partial C_3}{r\ \partial \mathrm{r}}-k_{o2}C3C1-k_{o6}C_6C_3+k_{o1}C1C2-k_{\mathrm{total}}C3 \tag{18}$$

(4) The dichloramine $C4$:

$$v\left(\sqrt{f}\left[\left(2.15\ \log\frac{r_0-r}{r_0}+1.43\right)\right]+1\right)\frac{\partial C_4}{\partial x}$$
$$=D\frac{\partial^2 C_4}{\partial \mathrm{r}^2}+\frac{D\partial C_4}{r\ \partial \mathrm{r}}-k_{o3}C4C1-k_{o5}C4-k_{o7}C6C4+k_{o2}C3C1+k_{o4}C5-k_{\mathrm{total}}C4 \tag{19}$$

(5)the trichloramine $C5$:

$$v\left(\sqrt{f}\left[\left(2.15\ \log\frac{r_0-r}{r_0}+1.43\right)\right]+1\right)\frac{\partial C_5}{\partial x}$$
$$=D\frac{\partial^2 C_5}{\partial \mathrm{r}^2}+\frac{D\partial C_5}{r\ \partial \mathrm{r}}-k_{o4}C5+k_{o3}C4C1-k_{\mathrm{total}}C5 \tag{20}$$

(6) Ammoniacal nitrogen $C6$:

$$v\left(\sqrt{f}\left[\left(2.15\ \log\frac{r_0-r}{r_0}+1.43\right)\right]+1\right)\frac{\partial C_6}{\partial x}$$
$$=D\frac{\partial^2 C_6}{\partial \mathrm{r}^2}+\frac{D\partial C_6}{r\ \partial \mathrm{r}}-k_{o6}C3C6-k_{o7}C4C6+k_{o5}C4-k_{\mathrm{total}}C6 \tag{21}$$

4. Resolution procedure

One solves these types of set equations by adopting the explicit model scheme of finite difference scheme of Euler method. Discretizing axial and radial spaces, we write:

$x=i\ \Delta x$, $i=1, \ldots\ n$, and $\Delta x\in[10^{-1}\text{–}10^{-3}]$
$r=j\ \Delta r$, $j=1, \ldots\ m$, and $\Delta r\in[10^{-2}\text{–}10^{-3}]$

$$\frac{\partial C_k}{\partial x}=\frac{C_k(i+1,j)-C_k(i,j)}{\Delta x} \tag{22}$$

$$\frac{\partial C_k}{\partial r}=\frac{C_k(i,j+1)-C_k(i,j-1)}{2\Delta r} \tag{23}$$

$$\frac{\partial^2 C_k}{\partial r^2}=\frac{C_k(i,j-1)-2C_k(i,j)+C_k(i,j+1)}{\Delta r^2} \tag{24}$$

where the index k: is chlorine or the chlorine derivative or the nitrogen derivative. Thus one can express the complete discretized form obtained by gathering Eqs. (22)–(24), and the global Eq. (25) is only valid for nodes situated within the railing as follow:

$$v\left(\sqrt{f}\left[\left(2.15\ \log\frac{r_0-j\Delta r}{r_0}+1.43\right)\right]+1\right)\frac{C_k(i+1,j)-C_k(i,j)}{\Delta x}$$
$$=D\frac{C_k(i,j-1)-2C_k(i,j)+C_k(i,j+1)}{\Delta r^2}+\frac{D}{j\Delta r}\frac{C_k(i,j+1)-C_k(i,j-1)}{2\Delta r}+R_kC(i,j) \tag{25}$$

On the pipe center $r_0=0$, there is an indeterminacy form $0/0$ that we can surmount by application of HOPITAL's rule and the discretized equation for these nodes becomes:

$$v(\sqrt{f}\left[\left(2.15\ \log\frac{r_0-j\Delta r}{r_0}+1.43\right)\right]+1)\frac{C_k(i+1,j)-C_k(i,j)}{\Delta x}$$
$$=D\frac{C_k(i,j-1)-2C_k(i,j)+C_k(i,j+1)}{\Delta r^2}+RC_k(i,j) \tag{26}$$

Table 5 indicates the boundary conditions. Eq. (27) presents the assumption of axial symmetry on the centerline. Then the wall condition is presented by Eq. (28) where in treated water, the ammonia amount reacts with chlorine rapidly and quantitatively as shown in the Table 4 but kinetics constant of chlorine with wall is in order of greater 10^{-6}–$10^{-7}\,\mathrm{m\,s^{-1}}$ [22,23] for this reason k_w can be neglected comparing to K_b and thus assumed that is no chlorine reaction at the pipe wall. Finally, Eq. (29) assumes that the initial concentrations of chlorine and ammonia are not null and are equal to $C0$ and $N0$, respectively at the inlet of pipe.

The set of Eqs. (16)–(21) was simultaneously resolved by combination of the discretized expressions like Eqs. (25) and (26) with the use of the boundary

Table 5
Boundary conditions

at $r=0$: $\frac{\partial \mathrm{C}_1}{\partial \mathrm{r}}=0$; $\frac{\partial \mathrm{C}_2}{\partial \mathrm{r}}=0$; $\frac{\partial \mathrm{C}_{(3-6)}}{\partial \mathrm{r}}=0$	if $x\geqslant 0$	(26)
at $r=r_0$: $D\ \frac{\partial C_k}{\partial r}=0$ with $k=1, 2, 3, 4, 5$ and 6	if $x\geqslant 0$	(27)
at $x=0$: $C1=C0$; $C2=N0$; $C(3\text{–}6)=0$	if $0\leqslant r\leqslant r_0$	(28)

conditions. Next, one need to establish a program using the Fortran 1995 language to determine the concentrations of chlorine and chloramines at all pipe nodes $C_k(x, r)$. Furthermore, the cross sectional cup mixing average concentration where obtained by the applying the equation below:

$$C_{k\,av}(x) = \frac{\int_0^R C_k(r,x)Urdr}{\int_0^R v(\sqrt{f}[(2.15\log\frac{r_0-r}{r_0}+1.43)]+1)rdr} \tag{27}$$

Discretizing Eq. (30) then the application of a numerical method of integration such as Simpson's method on the radial axis leads to find the average concentration on the axial direction $C_k(x)$.

5. Results and discussion

The choice of observed rate constants of reactions of the formation and the hydrolysis k_{o3} and k_{o5} respectively, plays an important role in the shapes of concentration profiles. Values taken from Table 4 at operatory conditions case 1 of Table 6 are 0.97 and $1.17 \times 10^{-2}\,M^{-1}S^{-1}$, respectively, have not given good results owing to the bad selection of these observed rate constants (the results are not showed here). Hence, the suggested solution is to try several values of k_{o3} and k_{o5} recapitulated in Tables 2 and 5 in part I from precedent paper. In these conditions of pH and Temperature, there is an improvement in the concentration profiles, where the values of k_{o3} and k_{o5} are taken from Table 7 of the present part; these ones have also given good results (Fig. 3). The good selection of observed rate constants of set reactions contributes to closer of concentration profiles of experimental and predicted, however several used constants for Breakpoint reactions had not confirmed or found. Fig. 3 shows the profiles of disinfectant concentrations vs. molar ratio $C/N0$, where pH, $C0/N0$ and Ni values are 1.97, 7.20 and 0.95 mg/l, respectively, and these data are reported in Table 6. The monochloramine concentration decreases as the pipe axis distance increases, at the same time the dichloramine concentration rises to the maximum. Next, dichloramine decreases after the formation of trichloramine species, which is why the total chlorine concentration decreases along the pipe due to decreasing of concentrations of chloramines and the free chlorine residual, where it is observed that the predicted profiles are near to experimental profiles.

When, pH and $C0/N0$ are increasing to 7.6 and 2.77, and the initial concentration $C0$ of chlorine is doubled (from 1.34 to 2.02×10^{-4} M) and k_{o3} values lead to the curves of Fig. 4. Then the concentration of free residual chlorine in solution is doubled too. So the total chlorine concentration is high but the concentrations of monochloramine, dichloramine and trichloramine in solution are minimized. These simultaneity changes are due to rise of pH, the molar ratio value and k_{o3}, k_{o5}. This pH value is near to pKa_1, where the hypochlorous acid and the hypochlorite ion are present in equimolar amount; this enhances the disinfection process because the acid hypochlorous species is the strongest for bacteria destruction and the hypochlorous ion is more efficient for virus [72]. From the Table 6, the increasing of molar ratio is due to doubling of the initial concentration of chlorine and relatively for the initial ammonia concentration which is not really varied. Indeed, the additional amount of initial chlorine in solution improves the substitution reactions of chlorine with ammonia to produce chloramines, especially the monochloramine concentration decreases along the pipe where monochloramine is a less powerful disinfectant than free chlorine. This set of conditions pH, $C0/N0$ is going to maintain chlorine residual in pipe to guarantee bacteriological qualities in distributed water. This group of operatory conditions is compromised with the aim of disinfection because the increase of pH decreases the formation of trichloramine and improves the formation of nitrogen hydroxide (NOH), this molecule destructs chloramines formed during the substitution process consequently it enhances the elimination of chloramines in the solution [73,74].

The pursuit to increase the pH value to 8.10 and the decrease of molar ratio value to 1.94 and the diminution of initial chlorine concentration $C0$, these changes are shown in Fig. 5. It is noted that the concentration of free chlorine residual diminishes and the monochloramine concentration increases in

Table 6
Modelling data [9]

	pH	T, °K	Ni, mg/l	$N0$, mol/l	$C0/N0$	$C0$, mol/l
Cas 1	7.20	288.3	0.95	6.786×10^{-5}	1.97	$1.340\ 10^{-4}$
Cas 2	7.60	288.5	1.02	7.286×10^{-5}	2.77	$2.020\ 10^{-4}$
Cas 3	8.10	288.4	0.98	7.000×10^{-5}	1.94	$1.358\ 10^{-4}$

Table 7
k_{o5} and k_{o7} values as a function of pH [9]

pH values	K_{o3} $M^{-1}S^{-1}$	K_{o5} $M^{-1}S^{-1}$
7.20	20	$4.0\ 10^4$
7.60	40	$5.5\ 10^4$
8.10	100	$2.0\ 10^4$

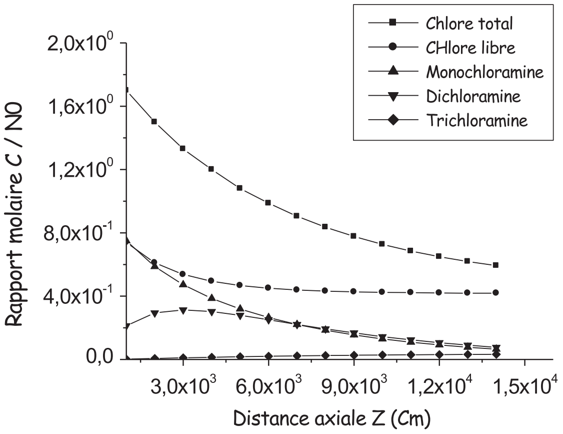

Fig. 3. Concentration profiles of chlorine and chloramines vs. $C/N0$ pH = 7.2, Ni = 0.95 mg/l and $C0/N0$ = 1.97.

solution that is explained by adequate operating conditions for monochloramine formation from the chlorine reaction with ammonia, a basic solution contributes to the monochloramine formation by the reaction of trichloramine with ammonia [75]. In addition, the stability of monochloramine leads to prevent the dichloramine formation; it also inhibits the production of monochloramine and the trichloramine from dichloramine. The constant k_{o3} is further doubled and the k_{o5} is taken about the half of the previous value of Table 7, this leads to accumulate the formation of chloramine where the diminution of free chlorine residual concentration in the solution occurs, so this group of conditions is disfavored for Breakpoint chlorination. It is important to find a compromise between pH, molar ratio and observed rate constants for improving the disinfection process and minimizing the differences between experimental and predicted profiles.

To sum up, these results have two main objectives. The first is the improvement on profiles, where the predicted profiles are near to the experimental profiles [9]. The second, several trials of conditions at pH 7.6, Ni = 1.02 mg/l and $C0/N0$ = 2.77 with other different combinations of observed constant rates are omitted due to the worst superpose of experimental profiles on predicted profiles. This optimization is going to prove the best operatory conditions that are the ones that give more free residual chlorine. These observations are depicted on the Fig. 4 where the operatory conditions are found the best.

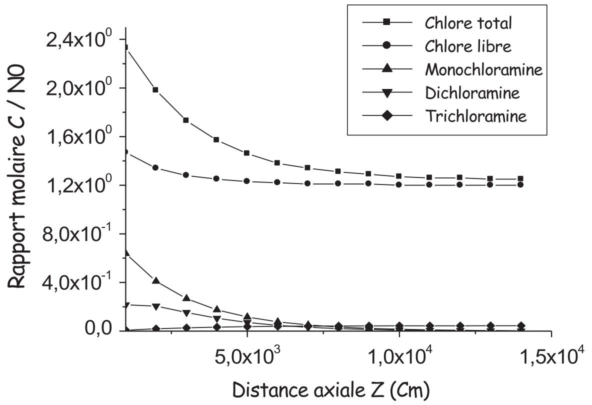

Fig. 4. Concentration profiles of chlorine and chloramines vs. $C/N0$ pH = 7.6, Ni = 1.02 mg/l and $C0/N0$ = 2.77.

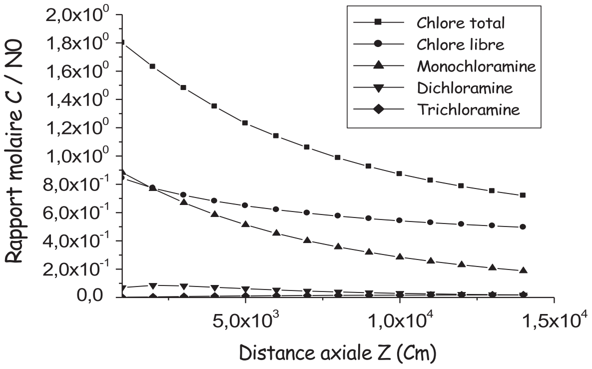

Fig. 5. Concentration profiles of chlorine and chloramines vs. C/N0 pH = 8.10, Ni = 0.98 mg/l and $C0/N0$ = 1.94.

6. Conclusion

This study shows that:

- During the final step of water treatment, the addition of chlorine serves to destruction of pathogen microorganisms owing to the presence of chlorine residual at or up the Breakpoint, where emerges a set of chlorine reactions with ammonia that are not defined precisely the reactions series presented at Breakpoint chlorination. From precedent paper (part I), we have obtained a model of set reactions of Table 2.
- The determination of constants of kinetics and observed rate constitutes another problem because there are not an agreement on these constant

expressions, their uses produce errors on results, this leads to several tries to obtain the required results. In other hand it is very important to express the influence of pH on the formations of monochloramine and dichloramine and trichloramine hydrolysis. The use of observed rate constants instead of Arrhenius expressions in chemical kinetics expressions $R_k(C)$ of transport equations should improve really the concentration profiles of monochloramine and dichloramine, these observed rate constants are not used or ignored in many works.

- Practice the disinfection at pH equal to 7.6 is more efficient than 7.2 and 8.10, this is due to increase the amount of free chlorine residual and minimizes the chloramines formation especially the monochloramine, this is also agree with the increase of initial molar ratio chlorine to ammonia.
- The increase of observed rate constants of the trichloramine formation and intermediate formation minimizes in one hand the chloramine and increase the free chlorine residual concentration and in other hand the difference between experimental and predicted profiles is diminished.
- The turbulent flow has given good results, because in this case the term of diffusion is not neglected, and the velocity distribution has expressed as a function of the pipe radius and friction factor, but the hypothesis of plug flow neglects the diffusion term and so the velocity distribution expression is different. The first supposition has given good results comparing with literature results.
- Through this study, the research of the best hypotheses to establish a modeling linking the changes in concentrations of chlorine and the chloramines need to set at least: the set of reactions, the observed rate expressions and the flow regime, their introductions have improved the predicted results by the minimizing of the differences of the experimental profiles and the predicted profiles found in this study.
- In the future studies, one determinates the influence of pH, temperature, initial molar ratio of chlorine to ammonia, various flow regimes and other observed rate constants of set reactions on the chlorine, ammonia, chloramines and intermediate species concentrations.

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Symbols

AOC — assimilable organic carbone
C — chlorine concentration, mol/l (M)
$C0$ — initial chlorine concentration, mol/l (M)
$C1$ — free chlorine concentration
$C2$ — ammonia concentration
$C3$ — monochloramine concentration
$C4$ — dichloramine concentration
$C5$ — trichloramine concentration
$C6$ — nitrogen hydroxide concentration, mol/l (M)
C_{av} — average concentration, mol/l (M)
CBPs — chlorination by-products
C_k — concentration of kth reactants, mol/l (m)
D — global diffusion coefficient, $cm^2\,s^{-1}$
d — pipe diameter, cm
D_{eddy} — Eddy diffusion coefficient, $cm^2\,s^{-1}$
D_L — longitudinal diffusion coefficient, $cm^2\,s^{-1}$
D_{mol} — mass transfer coefficient, $cm^2\,s^{-1}$
D_r — radial diffusion coefficient, $cm^2\,s^{-1}$
f — friction factor
$f(r)$ — flow parameter
HAAs — haloacetic acids
k — first order rate constant $lg^{-1}\,h^{-1}$
K_{a1} — hypochlorous acid constant
K_{a2} — ammonia acid constant
k_b — bulk water reaction constant, s^{-1}
K_{HCl} — chlorine Henry constant, $M\,atm^{-1}$
K_{HN} — ammonia Henry constant, $M\,atm^{-1}$
K_{Ck} — kinetic rate constant for kth species
k_{ok} — observed rate constant for kth species
k_{total} — overall reaction constant, s^{-1}
k_{W} — pipe wall solution reaction constant, s^{-1}
N — bacteria density in the water, l^{-1}
N_0 — initial bacteria density in the water, l^{-1}
$N0$ — initial ammonia concentration, mol/l (M)
$\mathrm{Pe_a}$ — axial Péclet number dimensionless $\left(=\frac{L\times U}{D}\right)$
$\mathrm{Pe_r}$ — radial Péclet number dimensionless $\left(=\frac{L\times D}{r_0^2\times U}\right)$
r — radial distance, cm
r_0 — pipe radius, cm
Re — Reynolds number dimensionless $(=\frac{v\times d}{v})$
R_k — kinetic expression term of k component
S_0 — consumed substances concentrations by disinfectant
T — temperature, °K
t — time, s
THMs — trichloromethanes
U — local velocity flow, $cm\,s^{-1}$
v — average velocity flow, $cm\,s^{-1}$
v_c — central velocity, $cm.s^{-1}$

x — axial distance, cm

Xi — concentration of ith species, mol/l (M)

Y — distance, cm ($= r - r_0$)

Y_0 — initial bacterial concentration, MPN/100 ml

Y_t — bacterial concentration after time, MPN/100 ml

Greek

λ — inactivation rate constant, $\text{lg}^{-1}\,\text{h}^{-1}$

μ — growth rate constant of the bacterial units in the water, h^{-1}

v — water kinematic velocity, m^2/s ($=1.139 \times 10^{-6}\,\text{m}^2/\text{s}$ at 15°C)

Δx — space step in the axial direction, cm

Δr — space step in the radial direction, cm

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