

# Investigation of chlorine wall decay in an old, decommissioned metallic pipe using a pipe section reactor

R. Tonev and G. Dimova

## ABSTRACT

The study investigates the kinetics of free chlorine depletion in tap water from the Sofia distribution network. The overall decay rates, the bulk reaction rate coefficient, the wall reaction rate coefficient and the influence of mass transfer have been determined in a laboratory pipe section reactor (PSR), testing an old decommissioned metallic pipe. In total, 23 series of experiments were performed under different initial free chlorine concentrations and different hydraulic conditions. The applicability of different chlorine decay mathematical models has been investigated. A new model was proposed, combining zero order bulk reactions and first order wall reactions, describing the laboratory results with Nash-Sutcliffe efficiency coefficients over 0.99. The obtained values for the wall reaction coefficient vary in the range 0.008–0.030 m/h, decreasing exponentially with increasing initial chlorine concentration.

**Key words** | bulk reaction coefficient, chlorine decay kinetics, laboratory studies, wall reaction coefficient

R. Tonev (corresponding author)

G. Dimova

Department of Water Supply, Sewerage, Water and Waste Water Treatment, University of Architecture, Civil Engineering and Geodesy,

No. 1, Hristo Smirnenki Blvd, 1164 Sofia, Bulgaria

E-mail: [radoslaw\\_tonew@abv.bg](mailto:radoslaw_tonew@abv.bg)

## INTRODUCTION

Chlorine disinfection is the most commonly used method in centralized water supply systems all over the world for ensuring microbiological safety of drinking water. One of its main advantages is that the residual free available chlorine, which is the sum of hypochlorite ions, hypochlorous acid and chlorine gas, acts as a secondary disinfectant. It provides a residual bactericidal effect that provides further drinking water protection in the pipe network. According to the World Health Organization standards, concentrations up to 5 mg/l of free chlorine do not present a health risk for the consumers (WHO 2017). The WHO recommends that the concentration of free chlorine at the beginning of the water supply system is at least 0.5 mg/l after 30 minutes' contact of the disinfectant with water. At the end consumer, the recommended concentration is at least 0.2 mg/l; if, however, the concentration is above 0.3 mg/l some individuals can experience unpleasant smell and taste of water.

doi: 10.2166/ws.2020.017

The maintenance of certain concentrations of free residual chlorine creates a challenge for the water operators, since its concentration is constantly changing through the water distribution network. The decay of free chlorine is associated with the occurrence of different chemical reactions in the bulk phase of the water and at the inner pipe walls (Rossman *et al.* 1994). The development of distribution network simulation models has proven to be a useful tool for predicting the concentration of residual chlorine in any point of the network at a given time. For the last 35 years, this field has been continuously augmented with the contributions of many researches, who strive to get more accurate results to be applied in drinking water supply management practice (Grayman 2018).

### Chlorine decay in pipes

The mathematical model proposed by Rossman *et al.* (1994) is the most commonly used so far for describing chlorine

decay in water pipelines, although other models have also been developed (Biswas *et al.* 1993; Huang & McBean 2007; Yang *et al.* 2008). The main assumption of the Rossman model is that chlorine decay occurs in two places: in the bulk flow and on the contact surface (or very close to it) between the water and the inner wall of the pipes. The main equation is (Rossman *et al.* 1994):

$$\frac{\partial C}{\partial t} = -v \cdot \frac{\partial C}{\partial x} - k_b \cdot C - \frac{k_f}{r_h} \cdot (C - C_w) \quad (1)$$

where  $C$  is the chlorine concentration,  $t$  is the elapsed time,  $v$  is the water velocity,  $x$  is the distance along the pipe,  $k_b$  is the bulk reaction coefficient,  $k_f$  is the mass transfer coefficient,  $r_h$  is the hydraulic radius and  $C_w$  is the chlorine concentration at the pipe wall. The left side of Equation (1) describes the changes of chlorine concentration at a given section of the pipeline. The first term on the right-side accounts for the advective flux, while the second and third terms are associated with the occurring bulk and wall decay reactions.

### Bulk reactions

Chlorine demand in water distribution systems is mainly affected by the temperature, the initial chlorine concentration, the presence of natural organic matter (NOM) often measured as total organic carbon (TOC), and the presence of some inorganic species, e.g. iron (Powell *et al.* 2000; Vieira *et al.* 2004). Bulk reaction kinetics are usually determined by the standard bottle test (Walski *et al.* 2003). The main equation for the chemical reaction rate used in the mathematical models is:

$$\frac{\partial C}{\partial t} = -k' \cdot C^n \quad (2)$$

where  $C$  is the chlorine concentration,  $k'$  is the apparent rate constant, as  $k' = k \cdot [\text{Reac}]^m$ , as  $k$  is the real rate constant and  $[\text{Reac}]$  is the concentration of the species that react with chlorine,  $n$  and  $m$  are reaction orders with respect to chlorine and  $[\text{Reac}]$ . The ' $n$ ' parameter has either a positive value or may be zero. Usually, the models assume simple first order reactions (Haas &

Karra 1984; Biswas *et al.* 1993; Rossman *et al.* 1994; Vasconcelos *et al.* 1997). In some cases, however, bulk reactions can also be described by zero order models (Walski *et al.* 2003; Devarakonda *et al.* 2010). Other works opined that bulk chlorine decay kinetics are better described by a parallel first order model. It is based on a prerequisite that fast and slow reacting species are present in water. In this case, the general process is determined by two components, each modelled with first order reactions (Haas & Karra 1984; Vieira *et al.* 2004). There are also other, more complicated models of higher order (e.g.  $n > 1$ ) which in some cases better predict chlorine concentration over time (Clark 1998; Kim & Kim 2017).

### Wall reactions

Chlorine wall decay is usually associated with the interaction of chlorine with existing biofilm, corrosion deposits and the pipeline material. Field approaches (Vasconcelos *et al.* 1997) and laboratory studies (Rossman *et al.* 2001; Digiano & Zhang 2005) have been used to investigate the kinetics of wall reactions. The lack of a standard method is due to the large variety of factors influencing the process. Some studies focus on the chemical and physico-chemical parameters of water (Kiene *et al.* 1998; Digiano & Zhang 2005; Rossman 2006); others focus on the age, material, diameter and roughness of the pipes (Zhang *et al.* 1992; Vasconcelos *et al.* 1997; Al-Jasser 2007) or on the hydraulic conditions inside the pipes (Digiano & Zhang 2005; Clark *et al.* 2010).

The theoretical background assumes that two parallel processes can limit chlorine wall decay: the mass transfer of the disinfectant from the water to the wall and the rate of the wall decay reaction. If the wall decay reaction rate and the rate of chlorine transport to the wall are the same, and the process is a first order reaction with respect to the chlorine concentration at the pipe wall  $C_w$ , then it can be described by Equation (3) (Rossman *et al.* 1994):

$$\frac{\partial C}{\partial t} = - \left( k_{b1} + \frac{k_f \cdot k_{w1}}{r_h \cdot (k_f + k_{w1})} \right) \cdot C \quad (3)$$

where  $k_{w1}$  is the first order wall reaction coefficient and the rest of the parameters are as in Equation (1).

If the chlorine wall decay is a zero order reaction, two cases can be considered: (1) the chlorine decay is limited by the rate of the pipe wall reactions (Equation (4.1)) and (2) the chlorine decay is ‘mass transport’-limited, when the chlorine concentration is reduced so rapidly that the rate of mass transfer is insufficient to restore it (Equation (4.2)) (Vasconcelos *et al.* 1997):

$$\frac{\partial C}{\partial t} = -k_{b1} \cdot C - \frac{k_{w0}}{r_h} \quad (4.1)$$

$$\frac{\partial C}{\partial t} = -\left(k_{b1} + \frac{k_f}{r_h}\right) \cdot C \quad (4.2)$$

Equations (3) and (4.2) can be also expressed by the following general form:

$$\frac{\partial C}{\partial t} = -K \cdot C \quad (5)$$

where  $K$  is the overall first order reaction coefficient;  $K = K_{b1} + K_{w1}$ , where  $K_{b1}$  and  $K_{w1}$  are the overall first order bulk and wall reaction coefficients. First order wall reactions are most commonly associated with the presence of organic growths on the pipe wall surface, whereas zero order reactions are associated with the interaction of chlorine with inorganic corrosion or iron products (Vasconcelos *et al.* 1997; Kiene *et al.* 1998).

The present study aims to investigate the free chlorine decay kinetics in an old, decommissioned section of metallic pipe from the water distribution network of the city of Sofia.

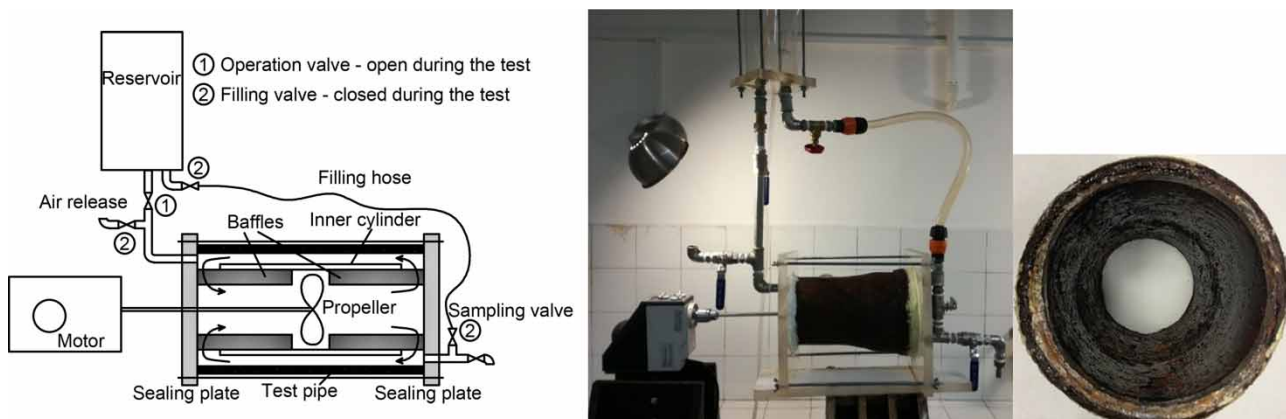
The study determines experimentally the overall decay rate ( $K$ ) and bulk reaction coefficient ( $k_b$ ) in laboratory conditions using tap water. The modelling of chlorine decay, for the specific case of the Sofia water system, is a necessary step for enhancing the control of disinfection, i.e. appropriate allocation of disinfection facilities and assurance of sufficient free residual chlorine in a network serving over 1.3 million consumers.

## MATERIALS AND METHODS

### Pipe section reactor

A laboratory pipe section reactor (PSR) was built, in accordance with the design of Digiano & Zhang (2005) (Figure 1).

An old iron-made pipe (internal diameter 150 mm,  $L = 300$  mm), decommissioned from the water distribution network of Sofia city, was used for the experiments. It was put into operation in the 1980s and was taken out of service in 2019. About 50% of the water supply network in Sofia consists of such pipes with similar characteristics. The sealing plates and the inner cylinder (diameter 120 mm) are made of acrylic. Eight rectangular shaped stainless steel baffles,  $B \times L = 20 \times 125$  mm, are attached to minimize the vortex in the annular space between the cylinder and test pipe. A propeller of diameter 100 mm and variable speed (up to  $600 \text{ r} \cdot \text{min}^{-1}$ ) creates a circulating flow through the annular space. To prevent random errors due to the occasional introduction of air into the PSR during manual



**Figure 1** | Scheme and photograph of the propeller reactor used in present work, including the decommissioned pipe.

sampling (Hua *et al.* 2017), the system was equipped with a top-up reservoir (Figure 1).

## Tests and measurement procedures

A series of experiments was made using tap water from the distribution system of Sofia city. Each experiment in the series included two parallel tests:

- Test 1: PSR test to determine the overall reaction coefficient ( $K$ );
- Test 2: Bottle test for evaluation of the bulk reaction coefficient ( $k_b$ ).

The model water solution was prepared with tap water and sodium hypochlorite, mixed in a sterilized, prewashed with chlorine-demand-free-water (Andrew *et al.* 1998) 10 l brown glass bottle. The tap water used was from the 'Losenetz reservoir' of the Sofia city water distribution system, which is fed by two different water sources, which are chlorinated several times before mixing in the storage reservoir. The temperature of the solution and the initial chlorine concentration were measured before each set of experiments. The PSR was filled with model water and a sample was taken to define starting condition. Then the propeller was started, which time was considered to be the beginning of the overall chlorine decay test. Samples were taken from the PSR at random time intervals. The experiment ended when the chlorine concentration in the PSR dropped below 0.05 mg/l. In parallel with the PSR tests, bottle tests were also performed. The rest of the model solution was poured into several 100 ml sterilized brown glass bottles, which had been prewashed with chlorine-demand-free-water. Each bottle was completely filled and closed with a polypropylene cap to prevent contact between the water and air. Bottles were stored in a dark environment with constant temperature, close to the temperature in the PSR. Simultaneously with the samples from the PSR, a sample from one of the small brown bottles was taken. Additional bottle tests were also performed to investigate the bulk reactions in greater detail.

For chlorine concentration, a standard DPD colorimetric method is used with sensitivity of  $\pm 0.02$  mg/l (HACH 2009). A thermometer with 0.1 °C reading intervals was used for temperature measurement. For other water

parameters of concern (e.g. iron, manganese, nitrites, ammonia and TOC), standard laboratory methods (HACH 2007) were used.

The flow velocity in the PSR was measured by detecting the flow travel for a certain time. For this purpose, a small piece of material with density close to water was placed in the PSR and the time for 10 full circuits was measured.

## RESULTS AND DISCUSSION

A linear relationship between the motor rotation speed ( $N$  r·min<sup>-1</sup>) and the average water flow velocity in the PSR ( $u_{av}$  m/s) was established. The velocity in the annular space,  $u$  m/s, was calculated based on the  $u_{av}$  and the cross-section area of the annular space for  $N = 200 \div 400$  r·min<sup>-1</sup>.

### Determination of overall chlorine decay rates ( $K$ , $K_b$ and $K_w$ )

In total, 14 series of experiments were performed with constant propeller rotation speed in accordance with annular flow velocity of  $u = 0.39$  m/s, and with different initial chlorine concentrations ranging from 0.30 to 1.80 mg/l. The average temperature of the tap water for all the tests varied within the range  $T = 11.3 - 13.9$  °C. For every single series of experiments, the temperature amplitude was below 2.0 °C.

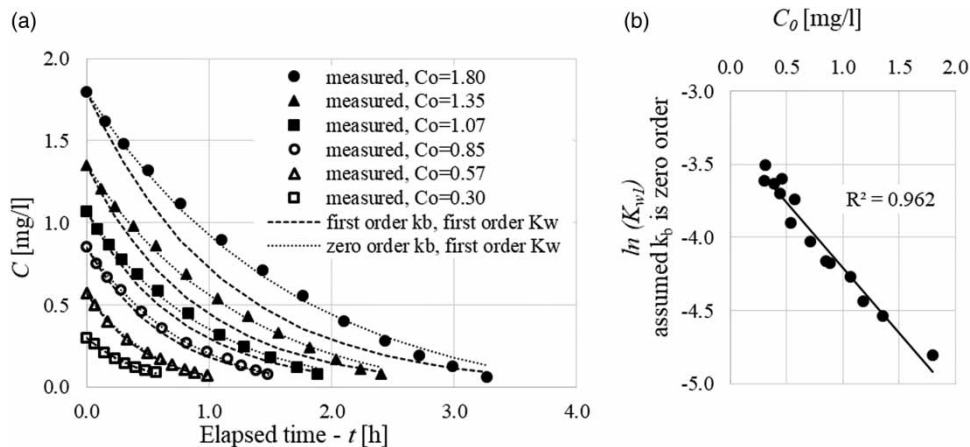
For an initial chlorine concentration  $C_0 \leq 0.85$  mg/l (Table 1, series 6–14) a general first order model (e.g. Equation (5)) describes very well the observed results. Since during the experiment the hydraulic conditions are constant, the temperature change is minor, and the annular flow velocity is constant;  $k_f$  can be considered a constant. In consequence, applying Equation (4.2),  $K_{w1}$  should also be constant. The results show, however, that  $K_{w1}$  varies in a relatively wide range – from 1.402 to 2.492 h<sup>-1</sup>. This leads to the conclusion that a mass transfer limited model (e.g. Equation (4.2)) does not describe appropriately the experimental results. At higher initial concentrations (Table 1, series 1–5), by applying the general first order model (e.g. Equation (5)), the difference between the calculated and observed value reaches 0.24 mg/l (Figure 2(a)) and the

**Table 1** | Parameters of assumed mathematical models for pipe section reactor series

Series no.	$C_0$ mg/l	$k_{b1}^b$ 1/h	$K$ 1/h	$K_{w1}$ 1/h	MAE <sup>a</sup>	NSE	$k_{b0}^b$ (mg/l)/h	$K_{w1}$ 1/h	MAE <sup>a</sup>	NSE
1	2	3	4	5	6	7	8	9	10	11
1	1.80	0.047	0.916	0.869	0.12	0.936	0.081	0.607	0.03	0.996
2	1.35	0.055	1.108	1.053	0.07	0.959	0.073	0.794	0.02	0.997
3	1.18	0.066	1.196	1.129	0.05	0.968	0.078	0.878	0.01	0.998
4	1.07	0.045	1.295	1.250	0.04	0.979	0.047	1.037	0.01	0.997
5	0.88	0.072	1.445	1.373	0.03	0.982	0.063	1.138	0.01	0.998
6	0.85	0.132	1.534	1.402	0.02	0.993	0.109	1.154	0.01	0.999
7	0.71	0.094	1.669	1.575	0.02	0.988	0.067	1.323	0.01	0.999
8	0.57	0.144	2.111	1.966	0.00	0.999	0.081	1.761	0.00	0.999
9	0.54	0.110	1.793	1.683	0.01	0.995	0.061	1.502	0.00	0.998
10	0.46	0.153	2.645	2.492	0.02	0.979	0.074	2.030	0.01	0.997
11	0.44	0.125	2.204	2.078	0.01	0.993	0.056	1.830	0.00	0.999
12	0.39	0.110	2.263	2.153	0.01	0.994	0.044	1.956	0.00	0.997
13	0.31	0.168	2.537	2.369	0.00	0.994	0.053	2.228	0.00	0.994
14	0.30	0.168	2.194	2.026	0.00	0.995	0.053	1.998	0.00	0.995

<sup>a</sup>MAE, mean absolute error; NSE, Nash-Sutcliffe efficiency coefficient.

<sup>b</sup>The different values for  $k_b$  during the experiment are explained with the changing properties of real tap water due to mixing of two sources in the feeding reservoir, being several times chlorinated before reaching the tap.

**Figure 2** | (a) Measured and predicted concentrations and (b) observed relationship between initial chlorine concentration and first order overall wall coefficient.

average absolute error is  $\geq 0.02$  mg/l, which is the sensitivity level of the laboratory method for chlorine measurement.

In conclusion, all experiments show a non-linear relationship (e.g. first order reaction model) for the chlorine decay in the PSR. First order wall reactions are observed in previous studies for ductile iron pipes (Rossman *et al.* 2001; Digiano & Zhang 2005) and for steel pipes (Al-Jasser 2007).

The obtained results also indicate that wall reactions have much greater impact than bulk reactions for the tested pipe fragment. A similar conclusion was also reached by Digiano & Zhang (2005) and Rossman (2006).

The obtained results suggest, however, that the general first order reaction model (Equation (5)), except for the mass transfer limited model (Equation (4.2)), can predict

accurately enough the chlorine decay reaction in the tested pipe only if the initial chlorine concentration is  $\leq 0.85$  mg/l. It should be noted that the model used for bulk reactions is simple first order. The same model was used in previous studies (Kiene *et al.* 1998; Rossman *et al.* 2001; Hallam *et al.* 2002; Digiano & Zhang 2005; Al-Jasser 2007); however, no information was found regarding how changes in the initial chlorine concentration might have affected the accuracy of the obtained results. In this study for the Sofia water supply system, where different initial chlorine concentrations were used (Table 1, column 2), the authors suggest that a bulk reaction rate of different order might describe better the bulk chlorine decay.

A new mathematical model is proposed, assuming that the bulk chlorine decay rate is a zero order reaction and the wall chlorine decay rate is a first order reaction. The general equation describing the process has the following differential and integral form:

$$\frac{\partial C}{\partial t} = -k_{b0} - K_{w1}.C \quad (6.1)$$

Considering that under initial conditions  $t = 0$  the chlorine concentration is  $C_{(t=0)} = C_0$ :

$$C_t = C_0.e^{-K_{w1}.t} - \frac{k_{b0}}{K_{w1}}.(1 - e^{-K_{w1}.t}) \quad (6.2)$$

Values of  $K_{w1}$  are calculated using least-squares regression analysis (Table 1, column 9). For all the series, except one, the mean absolute error is  $\leq 0.02$  mg/l, which is comparable to the measurement error (Table 1, column 10). The average Nash-Sutcliffe efficiency coefficient is 0.997, which implies better convergence than the first order general model, where the average NSE is 0.982 (Figure 2(a)). It is important to mention that both zero and first order models describe very well the bulk reactions, as also noted by other researchers (Devarakonda *et al.* 2010).

An exponential decrease in the value of  $K_{w1}$  was found as  $C_0$  increases (Figure 2(b)), after applying Equation (6.2). Since the mass transfer coefficient  $k_f$  is constant, such dependence can only be explained by a change in the rate coefficient of wall reactions  $k_{w1}$ . A similar trend has been observed by other authors (Hallam *et al.* 2002; Rossman

2006). Chlorine reaction with iron containing materials results in oxidation of the ferrous ion ( $\text{Fe}^{2+}$ ) to the ferric ion ( $\text{Fe}^{3+}$ ), which latter precipitates as ferric hydroxide (Vieira *et al.* 2004). This creates a protective layer on the inner pipe-wall surface, which is the main source of  $\text{Fe}^{2+}$  ions (Digiano & Zhang 2005). Depending on the hydraulic conditions, shear stress can occur at the inner wall of the pipe. The corroded material (i.e. the ferric hydroxide) is sheared off, resulting in the exposure of additional sections of the metal pipe to chemical interaction (Furnass *et al.* 2013). This process leads to a change in the ratio between the fast and slow reacting with chlorine species. At low initial chlorine concentration, the reaction rate would be determined only by the concentration of the fast-acting agents, while at higher  $C_0$  the slow-acting ones will also affect the process.

### Bulk reaction coefficient ( $k_b$ )

Four additional bottle tests were performed at temperature 13–14 °C to investigate the bulk reaction kinetics. The tap water quality analyses showed the presence of total manganese  $\text{Mn} = 0.008$  mg/l, ammonium  $\text{NH}_4^+ = 0.021$  mg/l and total organic carbon  $\text{TOC} = 2$  mg/l. The concentration of total iron and nitrite were below the detection limits, respectively  $< 0.02$  and  $< 0.05$  mg/l.

In all the tests, similar kinetics of chlorine decay was observed, which could be divided into two phases (Figure 3). The first phase, with a duration of about 5 hours, shows a significantly faster chlorine decay than the second phase. Simple and parallel first order models were applied to determine the bulk chlorine decay coefficients (Table 2). A regression and least squares regression analyses were performed accordingly. It can be concluded that the parallel first order model describes more accurately the experimental results (Figure 3 and Table 3, columns 1–6).

In addition, a parallel zero order model is proposed, expressed by the following integrated equations:

$$C_i = C_0 - (k_{b0,I} + k_{b0,II}).t_i; t_i \leq t_1 \quad (7.1)$$

$$C_i = C_0 - k_{b0,I}.t_1 - k_{b0,II}.t_i; t_i > t_1 \quad (7.2)$$

where  $C_i$  is the concentration of chlorine at time  $i$ ,  $k_{b0,I}$  and  $k_{b0,II}$  are reaction rate coefficients, respectively, for the first

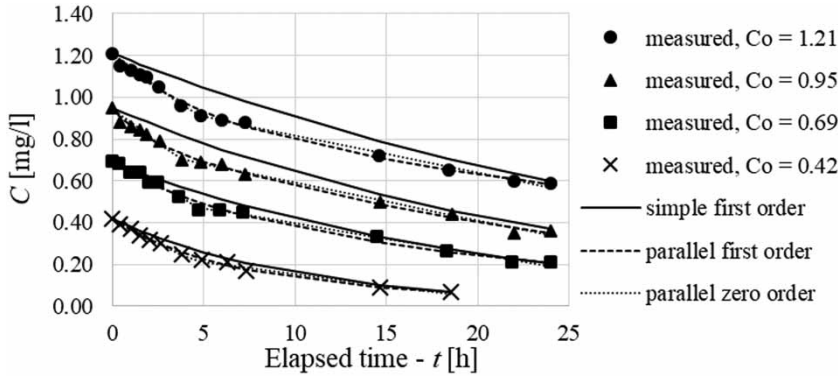


Figure 3 | Chlorine concentration decay in additional, 24 h bottle tests.

Table 2 | Bulk reaction mathematical models used in the present work<sup>a</sup>

Model	Differential equation (dC/dt=)	Integrated equation	Adjustable parameters
Zero order	$-k_{b0}$	$C = C_0 - k_{b0} \times t$	$k_{b0}$
Simple first order	$-k_{b1} \times C$	$C = C_0 \times e^{-(k_{b1} \cdot t)}$	$k_{b1}$
Parallel first order	$-k_{b1,I} \times C_1 - k_{b1,II} \times C_2$ , where $C_1 = C_0 \cdot x$ and $C_2 = C_0 \cdot (1 - x)$	$C = C_0 \cdot x \cdot e^{-(k_{b1,I} \cdot t)} + C_0 \cdot (1 - x) \cdot e^{-(k_{b1,II} \cdot t)}$	$k_{b1,I}; k_{b1,II}; x$

<sup>a</sup> $k_{b0}$  is the zero order bulk reaction coefficient,  $k_{b1}$  is the first order bulk reaction coefficient,  $k_{b1,I}$  and  $k_{b1,II}$  are the first order bulk reaction coefficients in the parallel model,  $x$  is the fraction of the initial chlorine concentration, related with fast reacting species,  $C_0$  is initial chlorine concentration.

Table 3 | Parameters of assumed mathematical models for bottle tests

$C_0$ mg/l	Parallel first order			MAE	NSE	Parallel zero order			MAE	NSE
	$k_{b1,I}$ 1/h	$k_{b1,II}$ 1/h	$x$			$k_{b0,I}$ (mg/l)/h	$k_{b0,II}$ (mg/l)/h	$t_1$ h		
1	2	3	4	5	6	7	8	9	10	11
0.42	0.237	0.069	0.43	0.00	0.997	0.035	0.011	4.28	0.01	0.993
0.69	0.249	0.041	0.20	0.01	0.990	0.031	0.015	4.75	0.01	0.995
0.95	0.578	0.035	0.14	0.01	0.993	0.050	0.018	3.53	0.01	0.992
1.21	0.248	0.020	0.22	0.01	0.994	0.048	0.018	4.49	0.01	0.995

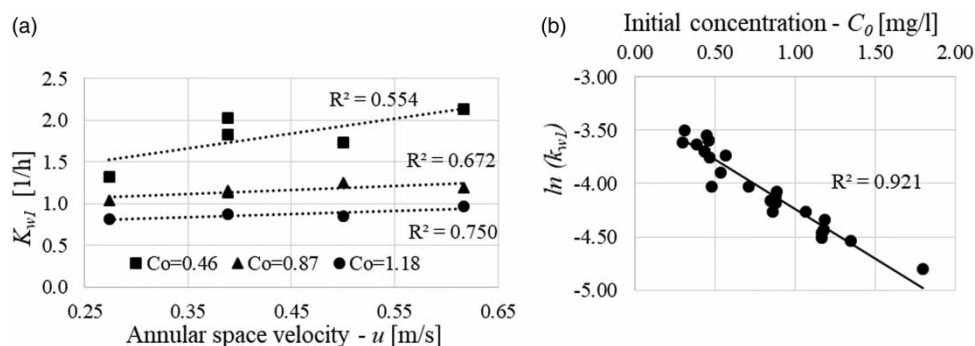
and second phase,  $t_i$  is the elapsed time from the beginning of the test and  $t_1$  is the elapsed time up to the end of the first phase. The adjustable parameters  $-k_{b0,I}$ ,  $k_{b0,II}$  and  $t_1$  are calculated by least squares regression analyses (Table 3, columns 7–9).

The values for the overall zero order bulk decay coefficient ( $K_{b0} = k_{b0,I} + k_{b0,II}$ ) obtained during the first 3.5–4.8 hours of the bottle tests are in the range 0.046–0.068 mg/l.h<sup>-1</sup> (Table 3, columns 7–8). They correspond

well to the obtained values for the bulk decay coefficient during the PSR series, which are in the range of 0.044–0.109 mg/l.h<sup>-1</sup> (Table 1, column 8).

### Wall reaction coefficient ( $k_{w1}$ )

In order to evaluate the first order wall reaction coefficient,  $k_{w1}$ , nine additional series of experiments were performed in the PSR with initial chlorine concentrations  $C_0 = 1.18; 0.87$



**Figure 4** | (a) Overall first order wall reaction rate at varying water velocity and (b) wall reaction rate coefficient by different initial chlorine concentration and different annular space velocities.

and 0.46 mg/l ( $\pm 0.02$ ) and annular space velocities of  $u = 0.27$ ; 0.50 and 0.62 m/s. The results were compared with the previous series of experiments with  $u = 0.39$  m/s (Table 1). The overall wall reaction rate,  $K_{w1}$ , is calculated using Equation (6.2).

The obtained results indicate that  $K_{w1}$  does not change significantly at  $u \geq 0.39$  m/s for the tests with similar initial chlorine concentration. The difference between the maximum and the minimum calculated value, relative to the minimum at  $C_0 = 1.18$ ; 0.87 and 0.46, is respectively 13.6%; 9.9% and 23.2%. In some cases, a higher velocity leads to a lower value of the overall wall reaction rate, and obversely. At lower water velocity, i.e.  $u = 0.27$  m/s, there is a clear tendency for lower values of  $K_{w1}$  compared to other results. This might be the consequence of a lower shear stress at the water-pipe contact surface. Therefore, an assumption can be made that mass transfer does not play a significant role in the chlorine decay process in the laboratory PSR. This statement is supported by other researchers, using similar laboratory reactors for determining chlorine decay kinetics. Digiano & Zhang (2005) and Al-Jasser (2007) concluded that the hydraulic conditions in the annular space of the PSR provide a continuous flow of chlorine to the pipe wall, so that the transport of chlorine is no longer a function of mass transfer. In consequence, the wall reaction coefficient can be calculated using the following equation:

$$K_{w1} = \frac{k_{w1}}{r_h} \quad (8)$$

Given the design of the PSR and the way the water flows inside, the hydraulic radius would be the ratio between the cross-sectional area of the annular space and the inner perimeter of the test pipe; that is,  $r_h = 0.0135$  m. The values of  $k_{w1}$  for all 23 series vary in the range of 0.008–0.030 m/h (Figure 2(b)). This range corresponds well with the values, obtained by other authors, i.e. 0.001–0.065 m/h, summarized in Rossman (2006).

Previous studies concluded that with the increase of water velocities, chlorine wall demand also increases (Grayman *et al.* 2002; Doshi *et al.* 2003; Clark & Haught 2005). The results of the current study show however, that the initial chlorine concentration also significantly influences the chlorine wall decay process (Figure 4(a)).

## CONCLUSIONS

The free chlorine decay in an old metallic pipe was investigated under laboratory conditions with tap water from the Sofia distribution system. The overall decay rates ( $K$ ,  $K_w$  and  $K_b$ ), the bulk reaction rate coefficient ( $k_b$ ), the wall reaction rate coefficient ( $k_w$ ) and the influence of the mass transfer process have been determined based on a series of experiments. The laboratory pipe section reactor, being a closed homogenous system, is suitable for the study of the kinetics of chlorine decay in water.

It can be concluded that a first order general model is applicable for predicting overall chlorine decay rates ( $K$ ,  $K_w$  and  $K_b$ ) at lower initial concentrations (0.3–0.85 mg/l)



for the tested specific conditions from the Sofia water supply system; however, the model is not appropriate for describing the laboratory results at higher initial chlorine concentrations (0.88–1.8 mg/l).

With regard to the chlorine decay bulk reactions, a first order parallel model characterizes well the tested tap water. The proposed zero order parallel model, however, describes even better the laboratory results, having Nash-Sutcliffe efficiency coefficients over 0.99.

The first order wall reaction model is appropriate for predicting the wall reaction decay in the studied metallic pipe. The respective wall reaction coefficient ( $k_{w1}$ ) has been determined for different initial chlorine concentrations (0.3–1.8 mg/l) and different hydraulic conditions (velocities of 0.27 m/s, 0.39 m/s, 0.50 m/s and 0.62 m/s). There is a clear trend of decreasing  $k_{w1}$  (from 0.03 to 0.008 m/h) with the increase of the initial chlorine concentration.

## ACKNOWLEDGEMENTS

This investigation was made within the framework of Contract No. Д - 92/16 of CNIP at UACEG. The authors would like to thank also the Sofijska Voda AD, part of Veolia Group, who contributed greatly to this research.

## REFERENCES

- Al-Jasser, A. 2007 Chlorine decay in drinking-water transmission and distribution systems: pipe service age effect. *Water Research* **41** (2), 387–396.
- Andrew, D., Clescerl, L., Greenberg, A. & Franson, M. 1998 *Standard Methods for the Examination of Water and Wastewater*, 20th edn. American Public Health Association, Washington, DC, USA.
- Biswas, P., Lu, C. & Clark, R. 1993 A model for chlorine concentration decay in pipes. *Water Research* **27** (12), 1715–1724.
- Clark, R. 1998 Chlorine demand and TTHM formation kinetics: a second-order model. *Journal of Environmental Engineering* **124** (1), 16–24.
- Clark, R. & Haught, R. 2005 Characterizing pipe wall demand: implications for water quality modeling. *Journal of Water Resources Planning and Management* **131** (3), 208–2017.
- Clark, R., Yang, Y., Impellitteri, C., Haught, R., Schupp, D., Panguluri, S. & Krishnan, E. 2010 Chlorine fate and transport in distribution systems: experimental and modeling studies. *Journal AWWA (American Water Works Association)* **102** (5), 144–155.
- Devarakonda, V., Moussa, N., VanBlaricum, V., Ginsberg, M. & Hock, V. 2010 Kinetics of free chlorine decay in water distribution networks. In: *World Environmental and Water Resources Congress 2010: Challenges of Change*, ASCE, pp. 4383–4392.
- Digiano, F. & Zhang, W. 2005 Pipe section reactor to evaluate chlorine-wall reaction. *Journal AWWA (American Water Works Association)* **97** (1), 74–85.
- Doshi, P. E., Grayman, W. & Guastella, D. 2003 Field testing the chlorine wall demand in distribution mains. In: *AWWA (American Water Works Association) Annual Conference*, June 15–19 proceedings, Anaheim, California. AWWA 2003
- Furnass, W., Collins, R., Husband, P., Sharpe, R., Mounce, S. & Boxall, J. 2013 Modelling both the continual erosion and regeneration of discolouration material in drinking water distribution systems. *Water Supply* **14** (1), 81–90.
- Grayman, W. 2018 History of water quality modeling in distribution systems. In: *1st International WDSA/CCWI Joint Conference*, July 23–25 proceedings 2018, Kingston, Ontario, Canada.
- Grayman, W., Rossman, L., Gill, M., Li, Y. & Guastella, D. 2002 Measuring and modeling disinfectant wall demand in metallic pipes. In: *EWRI Conference on Water Resources Planning and Management*, May 19–22 proceedings, Roanoke, VA. ASCE 2002.
- Haas, C. & Karra, S. 1984 Kinetics of wastewater chlorine demand exertion. *Journal WPCF (Water Pollution Control Federation)* **56** (2), 170–173.
- HACH 2007 *DR 2800 Spectrophotometer – Procedures Manual*, 2nd edn. HACH Company, Loveland, CO, USA.
- HACH 2009 *Chlorine, Free: USEPA DPD Method 8021*. HACH Company, Loveland, CO, USA.
- Hallam, N., West, J., Forster, C., Powell, J. & Spencer, I. 2002 The decay of chlorine associated with the pipe wall in water distribution systems. *Water Research* **36** (14), 3479–3488.
- Hua, P., Ma, S., Ding, W. & Zhang, J. 2017 Structure analysis of pipe section reactor for pipe-wall reaction: a computational fluid dynamics analysis approach. *Water, Air and Soil Pollution* **228**, 422.
- Huang, J. & McBean, C. 2007 Using Bayesian statistics to estimate the coefficients of a two-component second-order chlorine bulk decay model for a water distribution system. *Water Research* **41** (2), 287–294.
- Kiene, L., Lu, W. & Levi, Y. 1998 Relative importance of the phenomena responsible for chlorine decay in drinking water distribution systems. *Water Science and Technology* **38** (6), 219–227.
- Kim, H. & Kim, S. 2017 Evaluation of chlorine decay models under transient conditions in a water distribution system. *Journal of Hydroinformatics* **19** (4), 522–537.
- Powell, J., Hallam, N., West, J., Forster, C. & Simms, J. 2000 Factors which control bulk chlorine decay rates. *Water Research* **34** (1), 117–126.

- Rossman, L. 2006 [The effect of advanced treatment on chlorine decay in metallic pipes](#). *Water Research* **40** (13), 2493–2502.
- Rossman, L., Clark, R. & Grayman, W. 1994 [Modeling chlorine residuals in drinking-water distribution systems](#). *Journal of Environmental Engineering* **120** (4), 803–820.
- Rossman, L., Brown, R., Singer, P. & Nuckols, J. 2001 [DBP formation kinetics in a simulated distribution system](#). *Water Research* **35** (14), 3483–3489.
- Vasconcelos, J., Rossman, L., Grayman, W., Boulos, P. & Clark, R. 1997 [Kinetics of chlorine decay](#). *Journal AWWA (American Water Works Association)* **89** (7), 54–65.
- Vieira, P., Coelho, S. & Loureiro, D. 2004 [Accounting for the influence of initial chlorine concentration, TOC, iron and temperature when modelling chlorine decay in water supply](#). *Journal of Water Supply: Research and Technology-Aqua* **53** (7), 453–467.
- Walski, T., Chase, D., Savic, D., Grayman, W., Beckwith, S. & Koelle, E. 2003 *Advanced Water Distribution Modeling and Management*. Haestad Press, Waterbury, CT, USA.
- WHO 2017 *Guidelines for Drinking-Water Quality: Fourth Edition Incorporating the First Addendum*. World Health Organization, Geneva.
- Yang, Y., Goodrich, J., Clark, R. & Sylvana, L. 2008 [Modeling and testing of reactive contaminant transport in drinking water pipes: chlorine response and implications for online contaminant detection](#). *Water Research* **42** (6–7), 1397–1412.
- Zhang, R., Kiene, L., Wable, O., Chan, S. & Duguet, P. 1992 [Modelling of chlorine residual in the water distribution network of Macao](#). *Environmental Technology* **13** (10), 937–946.

First received 21 October 2019; accepted in revised form 21 January 2020. Available online 7 February 2020