Dependency of bulk chlorine decay rates on flow velocity in water distribution networks

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Abstract Understanding chlorine residual decay kinetics and the factors that influence them are essential for such current tasks as siting chlorination facilities, dosage optimisation, choice of sampling locations and frequencies, and general design and operational control of drinking water networks, increasingly accomplished with the help of simulation models.

Available constants for bulk chlorine decay are typically determined under static conditions. However, as for all fast reactions in water flows, chlorine consumption rates in drinking water pipes may be influenced by the existing mixing regimes, a function of flow turbulence, which is primarily controlled by flow velocity and pipe diameter.

Flow velocities vary greatly in space and time in water transmission and distribution systems; pipe diameters are seldom uniform. Although both variables are readily available in the currently available network analysis simulators that implement chlorine models, such variations are not accounted for. Instead, a single preset decay rate constant is generally used for describing chlorine residual consumption throughout an entire system.

In addition to highlighting how negligible PVC pipe wall chlorine consumption is, as such, this paper presents experimental evidence of a significant correlation between pipe flow velocity and bulk chlorine decay rates, and proposes a simple but effective approach to implement this dependency in current simulators.

Keywords Bulk decay rates; chlorine modelling; chlorine residual decay; water distribution

Introduction It is current practice in many countries around the world to use the disinfectant action of chlorine to counteract microbial regrowth in water transmission and distribution systems (WTDs). The chlorine residual in the networks must be kept above a prescribed minimum concentration for efficient disinfection, and within an adequate range for organoleptic acceptability and minimisation of halogenated by-product formation. However, chlorine tends to decay as it travels along the networks, mostly due to its reaction with organic compounds (predominantly humic materials) in the water, as well as to its interaction with pipe walls (Gatel et al., 1998; Vasconcelos et al., 1997).

Since chlorine controls the proliferation of suspended bacteria, its concentration in the transported water is widely used to describe microbiological quality in the modelling of WTDs. Conversely, chlorine-based network analysis models have been gaining ground as prime support tools for water quality-related purposes. Understanding chlorine decay kinetics, and the factors that influence them, are thus essential for such current modelling tasks as siting chlorination facilities, dosage optimisation, choice of sampling locations and frequencies, and general design and operational control of WTDs (Elton et al., 1995; Kumar et al., 1997; Lee and Deininger, 1992; Nace et al., 1997; Rossman et al., 1994).

Available constants for bulk and wall chlorine decay are typically determined under static conditions or inferred from differential network measurements (Biswas and Clark, 1993; Chambers et al., 1995; Powell et al., 1999, 2000). Network average values are widely
used and often adjusted or “calibrated” to generate the best match between observed and predicted values.

However, as for all fast reactions in water flows (Saylor and Sreenivasan, 1998), chlorine consumption rates in drinking water pipes may be expected to be influenced by the prevailing mixing regimes, a function of flow turbulence and, therefore, of flow velocity and pipe diameter and material. In fact, because chlorine reacts rather rapidly, its consumption may depict a diffusion-controlled reaction. In such reactions, reactants are spent at a rate that is faster than their rate of diffusion and, consequently, the reaction rate increases with the turbulent mixing rate until the diffusion-control limit is reached (Rice, 1985).

Owing to differences in pipes diameter and, particularly, to variations in flow velocity, turbulent mixing vary greatly in space and time in WTDS. Such variations may lead to changes in the chlorine residual decay rates, which are not accounted for in currently available chlorine models such as EPANET (Rossman, 2000) or Piccolo (SAFÉGE, 1999), despite the fact that velocity and diameter values are available throughout the simulations.

In addition to highlighting the negligibleness of PVC pipe wall chlorine consumption, as such, this paper presents experimental evidence of a significant correlation between pipe flow velocity and bulk chlorine decay rates, and proposes a simple but effective approach to implement this dependency in current simulators.

**Material and methods**

**Experimental set-up**

The effect of flow velocity in bulk chlorine decay rates was investigated in a 120 m long, 1” PVC pipe closed loop system fitted with a variable speed pump, air-release and purge valves, 5 sampling ports, flowmeter and a 200 mm long glass section for visual inspection. All pipe loop materials were new and had not been in contact with water previously to the experiments. Amending and sampling the test water were carried out by means of hypodermic needles inserted in $\varnothing$12 mm ports closed with butyl rubber stoppers. Additions to the system were done with a 0.1–250 mL min$^{-1}$ peristaltic pump (ERT, Lisbon). A 10 mL glass syringe was used to withdraw water samples.

Experiments were done at room temperature (20°C ± 1°C). Test water temperature did not vary more than 1°C. The temperature of the flowing water was measured with a glass thermometer inserted through the stopper of one of the sampling ports. Each experiment was started only after any air bubbles, whose presence might compromise the control of turbulence regimes in the circuit, were completely released from the water flowing at constant velocity (as confirmed through visual inspection). This was facilitated by a careful design to ensure a constant gradient between the lowest point (water purge) and the highest point (air release valve) of the test rig, and the absence of air-trapping irregularities. The system was kept filled with chlorinated water between experiments in order to maintain its inner walls passivated with respect to chlorine over the entire experimental period (3 months).

**Chemicals**

Deionised water (0.1 $\mu$S cm$^{-1}$) was used in the experiments and for solution preparation. System chlorine decay was studied in water buffered at pH 7 ± 0.1 with phosphate (1 mM). Chlorine was added to the test water as a sodium hypochlorite (4% active chlorine, Aldrich) solution, to make a starting concentration of 1.5 mg L$^{-1}$. To simulate the organic content of the water, humates (humic acid, sodium salt, techn., Aldrich), added in aqueous solution, were used at 5 mg L$^{-1}$, to make up a total organic carbon (TOC) concentration of around 5 mg L$^{-1}$. Phosphate salts and other reagents used in chlorine residual determinations (DPD ferrous titrimetric method; APHA et al., 1998) were of analytical grade.
Experimental procedures

Before each experiment, the circuit was thoroughly flushed with a volume of flowing deionised water making up at least four times that of the system (61 L). The system was then filled with buffered water and ran at 0.56 m s\(^{-1}\). After completely purging any air bubbles, chlorine was added during a complete flow cycle (e.g., 10 min. at 0.20 m s\(^{-1}\)) and its homogeneity was confirmed by analysing 4 samples taken at quarter-cycle intervals from the same sampling port.

Each experiment was started by setting the pump to the required flow velocity and by letting water run for periods of up to 1 h before adding the humates solution within a complete flow cycle. Chlorine decay was followed from the beginning of the experiments by determining its concentration in samples taken from a sampling port 20 m downstream of the port used for humates addition. At pre-set intervals, a set of three samples was withdrawn, one third of a flow cycle apart, thus enabling the evaluation of chlorine homogeneity in the flowing water and, therefore, of the representativeness of the sampling (Figure 1).

Results and discussion

At all tested flow velocities, none of the added chlorine was consumed during the initial period (up to 1 h) before adding humates. However, the chlorine residual consistently started to decay immediately after humates were added to the water. Thus, in contrast with the widely accepted “wall effect” concept (e.g., Vasconcelos et al., 1997), the pipe loop did not display any detectable demand for chlorine over significantly large periods. The reaction between chlorine and PVC virtually reached equilibrium during the resting periods and the walls remained oxidised, even after being intensively washed with non-chlorinated water.

Thermodynamics would suggest that some chlorine consumption towards complete equilibrium might remain during the experiments. However, the results indicated that any additional chlorine residual consumption by “passivated” PVC walls would occur rather slowly, probably at a time scale comparable to that of detectable corrosion. Since (i) chlorine is a strong oxidant that reacts quickly and (ii) in systems where chlorine residual is used, the pipe walls are permanently in contact with it, they are also likely to be kept “passivated” and, therefore, do not display any significant contribution to chlorine residual decay, irrespectively of pipe material. This obviously relates to the time scale under consideration in this paper, and not that of corrosion.

Figure 1 illustrates the results of a chlorine decay experiment for \(V = 0.40 \text{ m s}^{-1}\). The most utilised kinetic model to describe the chlorine reaction in WTDS is the first-order exponential with respect to chlorine concentration (e.g., Chambers et al., 1995; Powell et al., 2000; Rossman et al., 1994; Vasconcelos et al., 1997). It has therefore been used here as a suitable modelling framework, and Figure 1 displays one such curve fitted to the experimental data.

![Figure 1](https://iwaponline.com/ws/article-pdf/3/1-2/209/477681/209.pdf)

**Figure 1** Chlorine residual decay in water flowing at \(V = 0.40 \text{ m s}^{-1}\), with fitted 1st-order exponential
Table 1 shows the chlorine decay rate ($K'$) values observed for 1st order exponential curves fitted to chlorine measurements along time at different velocities, with the corresponding goodness of fit (represented by the $R^2$ value). The ratio of $K'$ to the static decay rate ($V = 0.00$ m s$^{-1}$), here denoted as $K'_0$, represents the relative error that is incurred in the exponential decay rate if the static value is used. The table also shows the Reynolds number, $Re = VD/\nu$ (D being internal pipe diameter [m] and $\nu$ the kinematic viscosity [m$^2$s$^{-1}$]), as a measure of hydrodynamic turbulence and a scale-up parameter.

A significant influence of flow velocity and, therefore, of turbulence on chlorine decay rates was observed, thus depicting the typical behaviour of a diffusion-controlled reaction (Rice, 1985). If the values of $K'/K'_0$ are plotted against flow velocity, as shown in Figure 2, there is evidence of a clear and important correlation. A linear regression between the two yielded a good fit ($R^2 = 0.95$), leading to an empirical expression of the type:

$$K'/K'_0 = 1 + a \cdot V$$  \hspace{1cm} (1)

with $a = 2.58$ m$^{-1}$ s in the present case, which doubles the value of $K'$ (relative to $K'_0$) for a velocity slightly above 0.40 m s$^{-1}$. For the magnitude of the effect to be better perceived, Eq. (1) can be couched as:

$$K' = K'_0 \cdot (1 + a \cdot V)$$  \hspace{1cm} (2)

The range of Re tested in the present research (Table 1) covered laminar and smooth into transition turbulent hydraulic regimes (1″ PVC pipe). Limitations in the equipment used did not allow exploration of a more extended range, which is the purpose of a further set of experiments using a different rig. However, the tested range is already partially representative of common water transmission and distribution system hydraulic conditions.

Table 1  First-order exponential chlorine decay rates ($K'$) observed at different velocities ($V$), showing goodness of fit ($R^2$), ratio to static decay rate ($K'_0$) and Reynolds number (Re)

<table>
<thead>
<tr>
<th>$V$ (m s$^{-1}$)</th>
<th>$K'$ [min$^{-1}$]</th>
<th>$R^2$</th>
<th>$K'/K'_0$</th>
<th>Re</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>-0.002560</td>
<td>0.957</td>
<td>1.00</td>
<td>0</td>
</tr>
<tr>
<td>0.10</td>
<td>-0.003583</td>
<td>0.902</td>
<td>1.40</td>
<td>2475</td>
</tr>
<tr>
<td>0.20</td>
<td>-0.004282</td>
<td>0.914</td>
<td>1.67</td>
<td>4950</td>
</tr>
<tr>
<td>0.30</td>
<td>-0.004559</td>
<td>0.825</td>
<td>1.78</td>
<td>7426</td>
</tr>
<tr>
<td>0.40</td>
<td>-0.004927</td>
<td>0.929</td>
<td>1.92</td>
<td>9901</td>
</tr>
<tr>
<td>0.48</td>
<td>-0.005362</td>
<td>0.903</td>
<td>2.09</td>
<td>11881</td>
</tr>
<tr>
<td>0.56</td>
<td>-0.006565</td>
<td>0.873</td>
<td>2.56</td>
<td>13861</td>
</tr>
</tbody>
</table>

Figure 2  Observed $K'/K'_0$ values as a function of flow velocity and a linear fit

$K'/K'_0 = 2.58 \cdot V + 1.00$

$R^2 = 0.94$
Scaling-up may thus be accomplished by re-writing Eq. (2) in terms of Re:

\[ K' = K'_0 \cdot (1 + a \cdot V) = K'_0 \cdot (1 + a \cdot \text{Re} \cdot \nu / D^*) \]  

\[ D^* \text{ being the tested pipe diameter (} D^* = 0.025 \text{ m). Replacing } a \text{ and } D^* \text{ with their values and } \nu \text{ back into Re, Eq. (3) yields the following generalised expression for any flow velocity } V \text{ and pipe diameter } D: \]

\[ K' = K'_0 \cdot (1 + b \cdot V \cdot D) \]

with parameter \( b = 103.20 \text{ m}^{-2} \text{ s} \) in the present case. This expression may enable the estimation of the actual bulk decay rate constant \( K' \) at any pipe across the system, given its diameter and flow velocity, once the statically determined (\( V = 0.00 \text{ m s}^{-1} \)) decay rate constant \( K'_0 \) is known.

The parameter values in the above relationships are obviously valid for the tested conditions only, where deionised water and commercial-grade humates were used. None the less, since fast reacting inorganic compounds (e.g., ammonia, ferrous iron, manganese ion) are often oxidized by chlorine during the disinfection process itself, and their chlorine demand is thus largely depleted before the water leaves the treatment plant, it is expectable that the decay of chlorine residual in the networks is essentially due to its reaction with humates. Therefore, the above observed \( a \) value may approach those occurring in many WTDS, within the tested Re range.

Although it remains to be confirmed whether the obtained correlation and the same type of relationship between \( K' \) and Re still stand at flow velocities and Re values above the tested range, the findings and the approach developed in this research, taking into account the influence of turbulence on chlorine decay rates, may lead to improvements in modelling chlorine residual evolution in WTDS, namely in the use of chlorine residual as a water quality parameter.

**Conclusions**

The results of the research described led to the following main conclusions.

- At least in new PVC pipes, the walls have no significant effect on chlorine consumption, irrespectively of flow velocity; given the fast reacting properties of chlorine and the fact that chlorine is permanently available for pipe wall oxidation, it is likely that the same applies to all the systems where this disinfectant residual is used, irrespectively of pipe material;
- Bulk chlorine residual consumption by humates is controlled by a diffusion-limited reaction. In many systems, chlorine decay rates may thus depend on flow turbulent mixing rates and, consequently, on flow velocities and pipe diameters;
- It is likely that the fixed decay rates that are currently used for describing the consumption of bulk chlorine residual throughout water transmission and distribution systems do not reflect the actual behaviour of chlorine in such systems;
- Given that chlorine demand due to fast reacting inorganic compounds (e.g., ammonia, ferrous iron) is often largely depleted during the disinfection process itself, it is possible that chlorine residual decay in drinking water networks is essentially due to its reaction with humic derivatives and occurs at varying rates that may be estimated from statically (\( V = 0 \)) determined (or tabulated) chlorine residual decay rate constants, by applying an empirical expression such as above described;
- Improvements in simulating chlorine residual evolution in transmission and distribution networks may be expected by re-evaluating the so-called “wall effect” concept and by approaching chlorine residual decay making use of empirical decay rates that account...
for the effect of turbulent mixing through the consideration of flow velocity and pipe diameter values.

Acknowledgements
The authors are grateful to Elsa Mesquita and Victor Napier for technical support, and to Prof. Maria João Rosa for determining the Aldrich humic acid TOC equivalents. This research was partly funded by the E.U. through INCO-DC Project No. IC18CT970136.

References